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Exposure and Risk Assessment for 1,2,4-Trichlorobenzene

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16. Abstract (Limit: 200 words)

This report assesses the risk of exposure to 1,2,4-trichlorobenzene. This study is part of a program to identify the sources of and evaluate exposure to 129 priority pollutants. The analysis is based on available information from government, industry, and technical publications assembled in June of 1981.

The assessment includes an identification of releases to the environment during production, use, or disposal of the substance. In addition, the fate of 1,2,4-trichlorobenzene in the environment is considered; ambient levels to which various populations of humans and aquatic life are exposed are reported. Exposure levels are estimated and available data on toxicity are presented and interpreted. Information concerning all of these topics is combined in an assessment of the risks of exposure to 1,2,4-trichlorobenzene for various subpopulations.

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AN EXPOSURE AND RISK ASSESSMENT FOR

1,2,4-TRICHLOROBENZENE

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FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. Assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. The risk assessment process integrates health effects data (e.g., carcinogenicity, teratogenicity) with information on exposure. The components of exposure include an evaluation of the sources of the chemical, exposure pathways, ambient levels, and an identification of exposed populations including humans and aquatic life.

This assessment was performed as part of a program to determine the environmental risks associated with current use and disposal patterns for 65 chemicals and classes of chemicals (expanded to 129 "priority pollutants") named in the 1977 Clean Water Act. It includes an assessment of risk for humans and aquatic life and is intended to serve as a technical basis for developing the most appropriate and effective strategy for mitigating these risks.

This document is a contractors' final report. It has been extensively reviewed by the individual contractors and by the EPA at several stages of completion. Each chapter of the draft was reviewed by members of the authoring contractor's senior technical staff (e.g., toxicologists, environmental scientists) who had not previously been directly involved in the work. These individuals were selected by management to be the technical peers of the chapter authors. The chapters were comprehensively checked for uniformity in quality and content by the contractor's editorial team, which also was responsible for the production of the final report. The contractor's senior project management subsequently reviewed the final report in its entirety.

At EPA a senior staff member was responsible for guiding the contractors, reviewing the manuscripts, and soliciting comments, where appropriate, from related programs within EPA (e.g., Office of Toxic Substances, Research and Development, Air Programs, Solid and Hazardous Waste, etc.). A complete draft was summarized by the assigned EPA staff member and reviewed for technical and policy implications with the Office Director (formerly the Deputy Assistant Administrator) of Water Regulations and Standards. Subsequent revisions were included in the final report.

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The materials balance for 1,2,4-trichlorobenzene (Chapter 3.0) was prepared by Acurex Corp. under Contract 68-01-6017 to the Monitoring and Data Support Division (MDSD), Office of Water Regulations and Standards (OWRS), U.S. Environmental Protection Agency. Steve Wendt was the task manager for Acurex, Inc. Patricia Leslie was responsible for report production.

John Segna of the Monitoring and Data Support Division was the project manager at EPA. Technical comments should be addressed directly to him.

1.0 TECHNICAL SUMMARY

The Monitoring and Data Support Division, Office of Water Regulations and Standards, U.S. Environmental Protection Agency, is conducting an ongoing program to identify the sources of, and evaluate the exposure to, 129 priority pollutants. This report assesses the exposure to and risks associated with 1,2,4-trichlorobenzene in the environment.

The conclusions reached in this assessment are summarized in this chapter. The potential risks are discussed within the constraints of available data, and the following subjects are also briefly discussed: human health effects; exposure routes and levels, where known; principal environmental pathways; toxic effects and exposure for aquatic biota; and the sources and volumes of releases of 1,2,4-trichlorobenzene to the environment (materials balance).

1.1 RISK TO HUMANS: EFFECTS, EXPOSURE AND FATE CONSIDERATIONS

The risk to humans resulting from exposure to 1,2,4-trichlorobenzene cannot be reliably evaluated at this time, due to the insufficiency of data in two areas. First, there is a general lack of data on the carcinogenicity, teratogenicity, mutagenicity and long-term oral toxicity of 1,2,4-trichlorobenzene. Second, there are limited data on the levels of the compound in all environmental media to which humans are exposed. The limited information that is available suggests that there is little risk associated with environmental exposure to 1,2,4-trichlorobenzene via inhalation, principally because the levels of the compound detected in the atmosphere are much lower than those estimated to cause adverse effects in humans. The highest atmospheric concentration reported, 100 ng/m^3 near a chemical plant, is 200,000 times lower than the no-effect level for eye and respiratory tract irritation in man (19 mg/m^3). The risk associated with ingestion of drinking water contaminated with 1,2,4-trichlorobenzene is uncertain; elevated levels of 1,2,4-trichlorobenzene are detected infrequently in drinking waters or in surface water near drinking water system intakes. However, in the absence of adequate effects data and monitoring information, the significance of these infrequent elevated levels of 1,2,4-trichlorobenzene to human health cannot be reliably determined.

1.1.1 Adverse Effects Levels

Available health effects data provide no suggestion of adverse effects resulting in humans from exposure to low levels of 1,2,4-trichlorobenzene such as those commonly detected in the environment. However, none of the available animal studies provided sufficient data for extrapolation of actual dose-response relationships to humans.

Animal data indicate that 1,2,4-trichlorobenzene is slowly absorbed from the gut, skin, and lung. Following absorption, the compound is metabolized to phenols which, in the conjugated form, are then excreted, principally via the urine.

Subchronic studies have been performed with rhesus monkeys. At levels of 25 mg/kg/day of 1,2,4-trichlorobenzene orally administered for 120 days, little effect on the liver, hematological parameters or clinical chemistries has been observed. At levels of 90 mg/kg/day, however, signs of toxicity occurred. When given 174 mg/kg/day, animals experienced lethality within 20 to 30 days. Similar results were observed for rats, rabbits, and dogs inhaling 1,2,4-trichlorobenzene in concentrations up to 800 mg/m^3, 7 hrs/day, 5 days/week for 30 exposures.

In humans, eye and respiratory tract irritation has been reported following exposure to a level of 24 mg/m^3 in the air, but not to a level of 19 mg/m^3. No other reported effects data for man could be found.

1.1.2 Exposure

Exposure to 1,2,4-trichlorobenzene via inhalation does not appear to be a significant route. The compound is detected infrequently, and then, typically at low concentrations found in localized areas. Although the compound has been observed at atmospheric concentrations of 10-100 ng/m^3 near several chemical plants, usually 1,2,4-trichlorobenzene either is not found in the atmosphere or it occurs at levels below limits of analytical sampling and analysis.

Exposure to 1,2,4-trichlorobenzene through ingestion of drinking water may occur infrequently. The compound has been detected in 10 samples from community drinking water supplies at a median concentration of 0.02 μg/l, with levels ranging from 0.01 to 10.0 μg/l. In effluents from industrial discharges, 1,2,4-trichlorobenzene has been found at concentrations of 500 μg/l and higher.

Percutaneous exposure is not expected to be particularly significant because the principal non-occupational source of 1,2,4-trichlorobenzene exposure to the skin is from the air, in which relatively low concentrations of the compound are observed, as discussed above.

1.1.3 Fate Considerations

The chemical 1,2,4-trichlorobenzene is released to all environmental media. The largest identified releases (52%) are to the aquatic environment [to Publicly Owned Treatment Works (POTWs) and directly to surface water]. The land is the second largest receiving medium (36%) and is a potentially significant pathway. Of the releases to the atmosphere (12%), little is believed to persist in the environment. High atmospheric concentrations of 1,2,4-trichlorobenzene appear to be associated solely with localized industrial activities and are of brief duration.

The compound, when detected, is found in low concentrations (below 100 μg/l) in ambient waters; all observations reported in EPA's STORET Water Quality System were below detection limits. Higher concentrations (up to 670 μg/l) were found infrequently in the ambient waters in the vicinity of discharges from POTWs, textile plants, and non-ferrous metal plants. Of the 1,2,4-trichlorobenzene released to surface waters, volatilization appears to be the strongest process competing for its removal. The rate of volatilization is largely dependent upon the presence of adsorbing matter (micro-organisms and suspended sediments) and the degree of aeration. In surface waters with a substantial amount of biomass and suspended organic sediment, biodegradation and other biological pathways are likely to become important.

At biological waste treatment facilities where there are high concentrations of suspended biota, it is likely that biodegradation will effectively remove most of the 1,2,4-trichlorobenzene. Under these circumstances, volatilization has been shown to be relatively insignificant. There are other types of wastewater treatment practices in use in addition to biological. Removal efficiencies associated with different treatment processes at POTWs in general vary from 13% to 100% removal.

Freshwater sediments frequently adsorb 1,2,4-trichlorobenzene. The extent to which this occurs depends upon the amount of organic matter in the sediment and the concentration of 1,2,4-trichlorobenzene in the overlying water. Consideration of the Freundlich equation indicates that a river with a 1,2,4-trichlorobenzene concentration of 0.1 mg/l will have an associated 1,2,4-trichlorobenzene concentration in surface sediment of approximately 20 mg per kg of sediment. Suspended sediment serves as a sink for some portion of the 1,2,4-trichlorobenzene in water, although biodegradation competes with sediment adsorption as a removal process.

A potential environmental pathway that could not be evaluated due to lack of data is the migration to groundwaters of 1,2,4-trichlorobenzene deposited on land. In a single groundwater contamination field study, groundwater adjacent to the site of an accidental spill of fluids containing 1,2,4-trichlorobenzene was sampled immediately following and then 2 years after the incident. The compound was initially found at a concentration of 500 μg/l in groundwater and at 1 μg/l two years later. Biodegradation of 1,2,4-trichlorobenzene in soil has been observed in the laboratory, but the rate of biodegradation in the environment and how it may affect migration of the compound to groundwater are not known.

Of the relatively small quantity of 1,2,4-trichlorobenzene released to air, most is expected to be photodegraded at a rate equal to the rate of release. The primary mechanism of photodegradation appears to involve photolytically generated hydroxyl radicals. Other mechanisms such as photochlorination and biphenyl formation are not expected to be significant.

The effect of intermedia transfers of 1,2,4-trichlorobenzene subsequent to initial discharges to receiving media has not been evaluated.

1.2 RISK TO NON-HUMAN BIOTA: EFFECTS, EXPOSURE, AND FATE CONSIDERATIONS

Most of the available toxicity data for aquatic species are for the other chlorinated benzenes rather than for 1,2,4-trichlorobenzene specifically. Furthermore, the data base concerning concentrations in environmental media is very limited. Hence, risk can not be evaluated fully at this time.

The limited monitoring data suggest that a 1,2,4-trichlorobenzene level of 30 µg/l (the only identified criterion for 1,2,4-trichlorobenzene which was established in the Soviet Union) is rarely exceeded in ambient waters. Furthermore, in the rare instances in which 1,2,4-trichlorobenzene is observed at elevated concentrations (500 µg/l or higher), it is likely that the 1,2,4-trichlorobenzene is rapidly volatilized or adsorbed by suspended sediment, decreasing its availability to aquatic organisms.

1.2.1 Toxic Effects

The levels of chlorinated benzenes at which acute toxic effects are shown to occur in different aquatic species range from 1 mg/l to 50 mg/l, with only one report of a level of 0.45 mg/l. Chronic effects are induced by these compounds at estimated levels of 200 to 700 µg/l.

1.2.2 Exposure

Ambient surface waters typically contain 1,2,4-trichlorobenzene at concentrations below 100 µg/l. The principal occurrence of elevated levels of 1,2,4-trichlorobenzene above the effects level is in localized areas near or adjacent to industrial plants or POTW discharges. In these localized areas, 1,2,4-trichlorobenzene has been observed at concentrations ranging from 0.01 µg/l to 500 µg/l in effluents from municipal and industrial wastewaters to as high as 2700 µg/l in selected untreated industrial effluents.

1.2.3 Fate Considerations

Of principal concern is the fate of 1,2,4-trichlorobenzene occurring at elevated concentrations near or downstream of industrial effluents. Based on results of environmental system simulation by the U.S. EPA's EXAMS model and based on information in the literature, volatilization is the most significant removal process of 1,2,4-trichlorobenzene from water. EXAMS indicated that as much as 90% of the chemical's loss was accounted for by volatilization, resulting in a system clearance time of 6.5 to 19 months. Some of the chemical is likely to be adsorbed by suspended sediment. The remainder is absorbed by micro-organisms, but probably at a concentration far lower than that near the point of initial entry into the aquatic environment. Thus it appears exceedingly unlikely that levels as high as 2700 µg/l (as reported above) will persist long enough to result in appreciable exposure to aquatic populations.

1.3 MATERIALS BALANCE

An estimated 5335 kkg of 1,2,4-trichlorobenzene were released to the environment in 1979. The largest release was to water (2804 kkg or 52%), with 42% of the total estimated release discharged to POTWs (2240 kkg) and 10% discharged directly to surface waters (534 kkg). The land is also the recipient of a major portion of 1,2,4-trichlorobenzene releases, receiving 1920 kkg or approximately 36% of the annual total. Only 12% of the total releases are made directly to the atmosphere.

Of the aquatic discharges, 2264 kkg are released to POTWs and 540 kkg to surface waters. The bulk of effluent discharge to POTWs is contributed by the textile industry, which utilizes 1,2,4-trichlorobenzene as a dyeing agent primarily for polyester fibers. This industry is the largest user of the chemical in the United States today, consuming 42.4% (3490 kkg) of the available U.S. supply. The only other identified sources of 1,2,4-trichlorobenzene releases to POTWs are the release of the chemical from electronic wafer degreasing operations and as a result of its use as a drain cleaner, although these are relatively minor; together these sources discharge 60 kkg to treatment systems, or 3% of the total discharge to POTWs. During the production of pesticides and functional, dielectric fluids bearing 1,2,4-trichlorobenzene, an estimated 7 kkg of 1,2,4-trichlorobenzene are released to POTWs from each process. No other aquatic discharges were identified.

The land receives the second largest total release of 1,2,4-trichlorobenzene totaling 1920 kkg each year. Approximately 71% of the total release to land occurs as a result of disposal of used electrical equipment containing 1,2,4-trichlorobenzene-bearing functional fluids. Following treatment of aquatic discharges, the textile industry disposes of 410 kkg (or 21% of total land releases) of 1,2,4-trichlorobenzene to the land in the form of sludges. Production of the compound is responsible for 3% of releases to land. The remaining 5% is from miscellaneous sources.

An estimated 611 kkg of 1,2,4-trichlorobenzene is released to the air annually. Use of 1,2,4-trichlorobenzene as a dye carrier accounts for 57% of total releases to air. Use of 1,2,4-trichlorobenzene as a chemical intermediate in the production of pesticides and functional fluids releases only small quantities to the atmosphere. The remaining 39% of the atmospheric releases of 1,2,4-trichlorobenzene are from miscellaneous uses including degreasing agents, septic tank and drain cleaners, wood preservative and abrasive formulations.

2.0 INTRODUCTION

The Office of Water Regulations and Standards (OWRS), Monitoring and Data Support Division, of the U.S. Environmental Protection Agency is conducting a program to evaluate the exposure to and risk of 129 priority pollutants in the nation's environment. The risks to be evaluated include potential harm to human beings and deleterious effects on fish and other biota. The goal of the task under which this report has been prepared is to integrate information and to estimate the risk based on receptor exposure to these substances. The results are intended to serve as a basis for developing suitable regulatory strategies for reducing the risk, if such action is indicated.

This report is intended to provide a brief, but comprehensive summary of the production, use, distribution, fate, effects, exposure to, and potential risks associated with 1,2,4-trichlorobenzene. Waterborne routes of exposure are stressed due to the emphasis of the OWRS on aquatic and water-related pathways.

The major problem associated with the exposure and risk evaluation of 1,2,4-trichlorobenzene arises from the general lack of data on both human effects and the concentrations of 1,2,4-trichlorobenzene occurring in the environment. Though ingestion of 1,2,4-trichlorobenzene in drinking water is a potential route of exposure, it is difficult to assess the risk because of insufficient effects data and knowledge of the frequency of exposure.

In the absence of extensive monitoring data, exposures have been evaluated on the basis of scattered observations in the literature and in the STORET Water Quality System and on the basis of fate models, field observations, and laboratory data. The lack of data on the health effects of 1,2,4-trichlorobenzene precluded, however, any quantitative assessment of the risks associated with the estimated exposures.

In order to place the risks of water-related exposure into perspective, exposure to 1,2,4-trichlorobenzene via inhalation has also been considered, and the associated risk is expected to be minimal if any at all. Atmospheric emissions are infrequent and the compound is not expected to persist in the air due to rapid photodegradation.

This report is organized as follows:

- Chapter 3.0 contains information on releases from the production, use, and disposal of 1,2,4-trichlorobenzene, including identification of the form and amounts released to each receiving medium at the point of entry into the environment.
- Chapter 4.0 considers the fate of 1,2,4-trichlorobenzene leading from its release into the environment until exposure of receptors. Reports of available data regarding concentrations detected in environmental media are also discussed.

- Chapter 5.0 discusses the adverse effects of 1,2,4-trichlorobenzene and identifies, where possible, concentrations eliciting these effects in humans, and quantifies the likely pathways and levels of human exposure.
- Chapter 6.0 considers the effects of 1,2,4-trichlorobenzene on biota and quantifies the environmental exposure of aquatic biota to the compound.
- Chapter 7.0 discusses the risk considerations for various subpopulations of humans and aquatic organisms.
- Appendices A and B present the assumptions and calculations for the estimated environmental releases of 1,2,4-trichlorobenzene described in Chapter 3.0. Appendix C presents the assumptions and calculations for volatilization in Chapter 4.0.

3.0 MATERIALS BALANCE

3.1 INTRODUCTION

This Chapter presents an environmental materials balance for 1,2,4-trichlorobenzene in the United States for the year 1979. It considers the major sources of 1,2,4-trichlorobenzene releases to water [publicly owned treatment works (POTWs) and surface water], land, and air, and estimates the amount contained in products for the year 1979. The flow of 1,2,4-trichlorobenzene from production, use, and disposal to the first point of entry into the environment is shown in Figure 3-1.

Approximately 89% of the 1,2,4-trichlorobenzene consumed in the U.S. in 1979 came from domestic production, nearly 11% was imported, and <1% was drawn from stocks. Most of the 1,2,4-trichlorobenzene consumed was used as a dye carrier (46%); other high-volume uses were pesticide formulations (29%), and functional fluids (18%).

The estimated quantities of 1,2,4-trichlorobenzene dispersed to water (POTWs and surface water), land, and air are shown in Figure 3-1. Of the estimated 2,800 kkg of 1,2,4-trichlorobenzene discharged to water, about 2,260 kkg were released to POTWs, while 540 kkg were discharged directly to surface waters. The largest source of 1,2,4-trichlorobenzene wastes discharged to POTWs and surface waters was the textile industry (2,190 kkg and 540 kkg, respectively). The largest source of 1,2,4-trichlorobenzene disposed of on land was obsolete electrical apparatus impregnated with 1,2,4-trichlorobenzene-containing functional fluids (1,370 kkg). Although these apparatus were manufactured in years prior to 1979, the 1,2,4-trichlorobenzene released to the terrestial environment is considered in the materials balance because it was released in 1979. The most significant source of 1,2,4-trichlorobenzene emissions to the atmosphere was the textile industry (350 kkg), followed in magnitude by degreasing operations (190 kkg).

3.2 PRODUCTION

Though different methods can be used to produce 1,2,4-trichlorobenzene (see Appendix A, Note 7 for further details), only the currently practiced method is discussed in this section. Presently, 1,2,4-trichlorobenzene is synthesized by the catalytic chlorination of 1,2- and 1,4-dichlorobenzene, with ferric chloride (or iron filings) as the catalyst (EPA 1977a).

Chlorobenzenes can be produced by either batch or continuous methods. Actual plant process data for the production of 1,2,4-trichlorobenzene are not available. However, on the basis of the process described by Ware and West (EPA 1977a) and on the low volume of domestic production (7,300 kkg in 1979), it is assumed that all 1,2,4-trichlorobenzene was produced via the batch method.

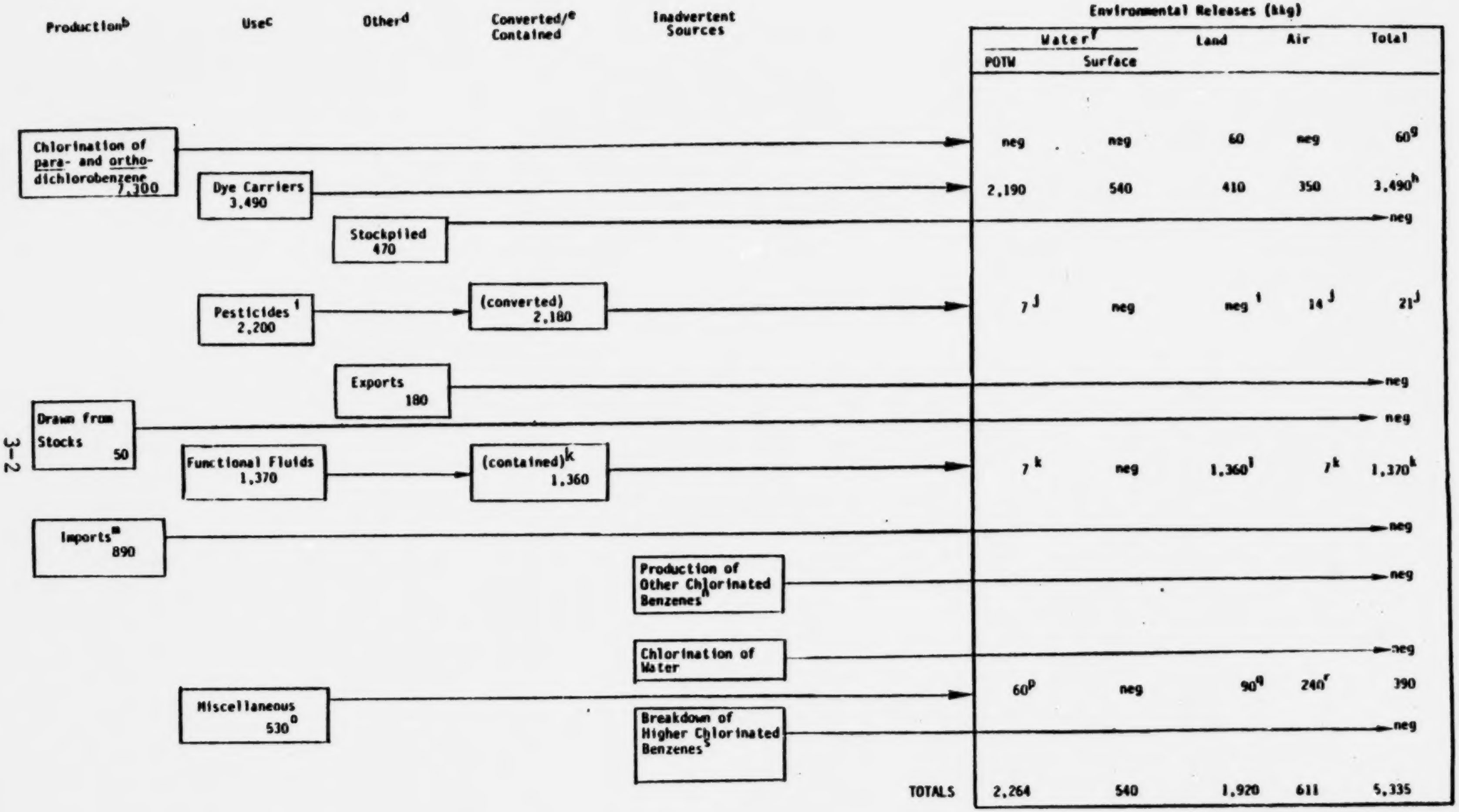

Production[b]
Use[c]
Other[d]
Converted/[e] Contained
Inadvertent Sources
Environmental Releases (kkg)
Water[f]
POTW
Surface
Land
Air
Total
Chlorination of para- and ortho-dichlorobenzene 7,300
Dye Carriers 3,490
Stockpiled 470
Pesticides[i] 2,200
(converted) 2,180
Exports 180
Drawn from Stocks 50
Functional Fluids 1,370
(contained)[k] 1,360
Imports[m] 890
Production of Other Chlorinated Benzenes[n]
Chlorination of Water
Miscellaneous 530[o]
Breakdown of Higher Chlorinated Benzenes[s]
neg neg 60 neg 60[g]
2,190 540 410 350 3,490[h]
neg
7[j] neg neg[i] 14[j] 21[j]
neg
neg
7[k] neg 1,360[l] 7[k] 1,370[k]
neg
neg
neg
60[p] neg 90[q] 240[r] 390
neg
TOTALS 2,264 540 1,920 611 5,335

Figure 3-1. Estimated Environmental Releases of 1,2,4-Trichlorobenzene from Production, Use and Inadvertent Sources, 1979 (kkg)[a]

Footnotes next page.

Figure 3-1. (continued)

a) Numbers may not add due to rounding; see text for discrepencies.

b) Total quantity of 1,2,4-trichlorobenzene domestically produced and withdrawn from inventory in 1979 was 7,301 and 46 kkg, respectively; see Appendix A, Note 1 for calculations.

c) Based on the following percentages of the total quantity of 1,2,4-trichlorobenzene consumed [i.e., (total quantity produced + drawn from stocks + imported) - (total quantity stockpiled + exported) or (7,300 + 46 + 886) - (466 + 177) = 7,589 kkg] by use from 1973 use pattern statistics: dye carriers (46%), pesticide production (29%), functional fluids (to include: synthetic transformer oil and dielectric fluids, 18%) and miscellaneous uses (to include: degreasing agents, septic tank and drain cleaners, wood preservatives and abrasive formulations, 7%) (Lewis, 1975; EPA, 1977a).

d) Hull and Co., 1980; assuming one-half of the 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene mix stockpiled and exported was 1,2,4-trichlorobenzene.

e) The majority (99%) of the 1,2,4-trichlorobenzene used to make pesticides was converted into other compounds (see text for further details; Sittig, 1977); 99% of the 1,2,4-trichlorobenzene-containing functional fluids manufactured in 1979 was contained within the electrical apparatus after manufacture, see text for further details.

f) Water is defined as either publicly owned treatment works (POTWs) or surface waters.

g) See Note 2, Appendix A for further details.

h) See Note 3, Appendix A for further details.

i) To include: dicamba, stirofos, and trichlorodinitrobenzene.

Figure 3-1. (concluded)

j) Based on process descriptions, 1% of the total quantity used is released to the environment where two-thirds of the release is emitted to the atmosphere and one-third is discharged to POTWs (Sittig, 1977).

k) Based on U.S. Patent information, 99% of the starting 1,2,4-trichlorobenzene is impregnated into the electrical apparatus and 1% is released to the environment. (See Note 4, Appendix A for further details.)

l) Assuming the quantity of 1,2,4-trichlorobenzene produced in 1979 and used in functional fluids for that year is equal to the quantity of 1,2,4-trichlorobenzene contained within electrical apparatus manufactured prior to 1979 which became obsolete and were disposed to land.

m) See Appendix A, Note 5 for calculations.

n) To include monochlorobenzene, ortho- and para- dichlorobenzene, the trichlorobenzenes (1,2,3- and 1,3,5-), the tetrachlorobenzenes (1,2,3,4-, 1,2,4,5- and 1,2,3,5-), pentachlorobenzene and hexachlorocyclohexane (lindane).

o) See footnote (c) for definition and Appendix A, Note 6 for quantities consumed and released by each component user.

p) An estimated 29 kkg of 1,2,4-trichlorobenzene discharged to POTWs from electronic wafer degreasing operations and 27 kkg from use as a drain cleaner (EPA, 1979c and Hull and Co., 1980).

q) An estimated 67 kkg of 1,2,4-trichlorobenzene disposed to land from electronic wafer degreasing operations and 27 kkg from use as a septic tank cleaner (EPA, 1979c and Hull and Co., 1980).

r) An estimated 190 kkg of 1,2,4-trichlorobenzene were emitted to the atmosphere from electronic wafer degreasing operations, 42 kkg from automotive engine cleaning, <1 kkg from wood preserving operations and 5 kkg from grinding wheel manufacture (EPA, 1979c; Hull, 1980; Hull and Co., 1980 and Richards, 1980).

s) To include: the tetrachlorobenzenes (1,2,3,4- 1,2,3,5- and 1,2,4,5-), pentachlorobenzene, hexachlorobenzene and hexachlorocyclohexane (lindane).

3.2.1 Chlorination of 1,2- and 1,4-Dichlorobenzene

Chlorobenzene and higher chlorinated benzenes are formed when chlorine reacts with benzene at slightly elevated temperatures in the presence of select catalysts:

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

$$C_6H_5 + Cl_2 \longrightarrow C_6H_4Cl_2 + HCl$$

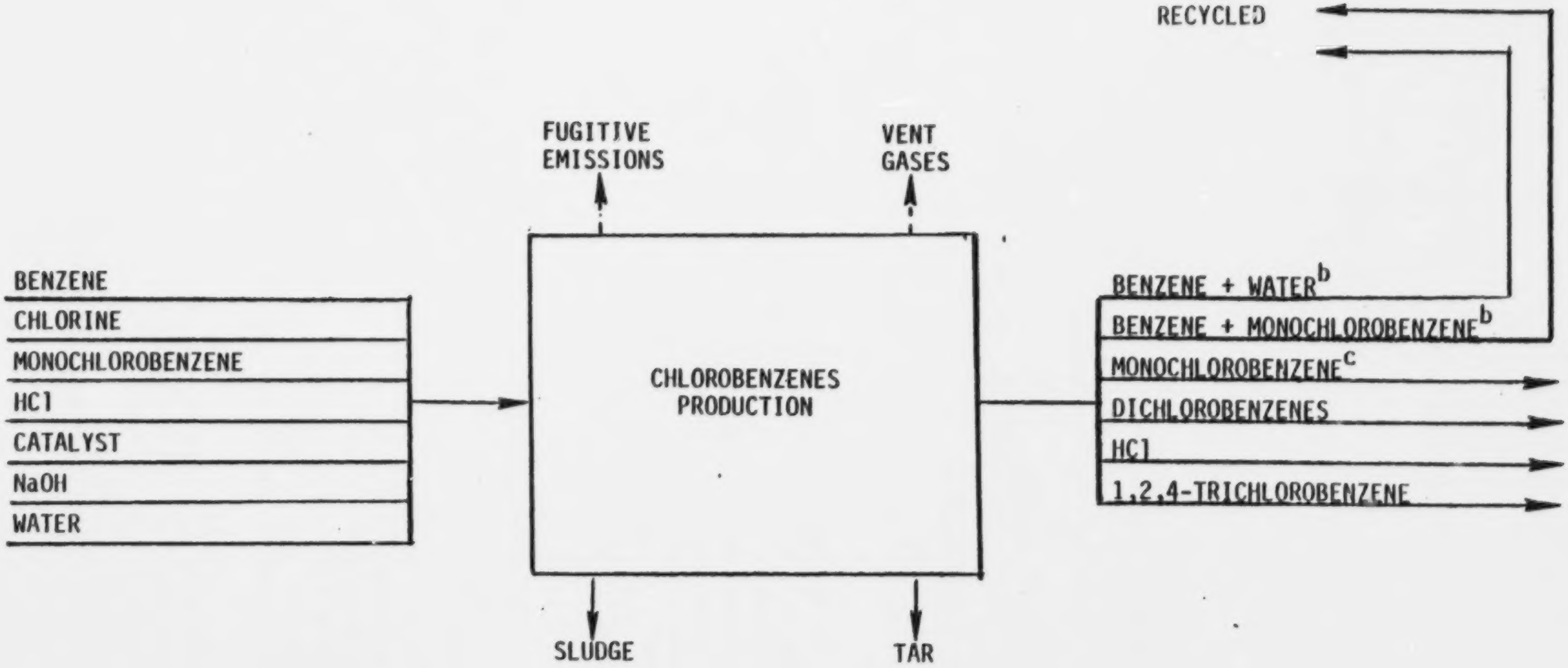
Once one chlorine atom has been substituted onto the benzene ring, further substitution takes place principally in the ortho and para positions (Morrison and Boyd 1979, see Appendix A, Note 8 for further details).

The 1,2- and 1,4-dichlorobenzene isomers are produced primarily from the distillation residues formed during chlorobenzene manufacture (EPA 1980a). The 1,2- isomer is chlorinated more rapidly than the 1,4- isomer to form 1,2,4-trichlorobenzene (along with minor quantities of 1,2,3-trichlorobenzene), which is easily separated from dichlorobenzene (and 1,2,3-trichlorobenzene) by fractional distillation (EPA 1977a and 1980a).

Figure 3-2 represents a simplified process for the production of 1,2,4-trichlorobenzene via the batch process (Lowenheim and Moran 1975; see Appendix A, Note 9 and Appendix B, Figure B-1 for further details). Benzene, chlorine, monochlorobenzene, hydrochloric acid, either anhydrous ferric chloride or iron turnings (as catalyst), sodium hydroxide, and water are added to the system to produce 1,2,4-trichlorobenzene. The products of the process are water, hydrochloric acid, benzene, chlorobenzene, 1,2- and 1,4-dichlorobenzene, 1,2,4-trichlorobenzene (liquid), waste emissions from the scrubber vent, and discharges from the separator and fractionation column.

During the production of 1,2,4-trichlorobenzene via the batch process, wastes are known to be generated at two points; sludges from the separator and tars from the fractionation column (see Appendix B, Figure B-1 for further details). To date, 1,2,4-trichlorobenzene has not been detected in the scrubber vent gases (EPA 1978a). Sludges generated by the separator are recycled for dichlorobenzene recovery and, therefore, their contribution to 1,2,4-trichlorobenzene releases into the environment is not expected be significant (EPA 1977a). Approximately 0.044 kkg of polychlorinated aromatic resinous material (tars) are generated by the fractionation column per metric ton of monochlorobenzene produced (EPA 1975a).

In 1978, nearly 136,960 kkg of monochlorobenzene were produced in the U.S. (USITC 1980). If one assumes that the quantity of monochlorobenzene produced in 1979 was similar to the volume for 1978 and that all of the monochlorobenzene was manufactured via the batch process, then about 6,000 kkg of polychlorinated aromatic resinous material (tars)


RECYCLED
FUGITIVE EMISSIONS
VENT GASES
BENZENE
CHLORINE
MONOCHLOROBENZENE
HCl
CATALYST
NaOH
WATER
CHLOROBENZENES PRODUCTION
BENZENE + WATER[b]
BENZENE + MONOCHLOROBENZENE[b]
MONOCHLOROBENZENE[c]
DICHLOROBENZENES
HCl
1,2,4-TRICHLOROBENZENE
SLUDGE
TAR

a) See Figure B-1 for further details.
b) Recycled for further processing.
c) Recovered and sent to storage as product.

Source: Lowenheim and Moran, 1975; EPA, 1977a.

Figure 3-2. Batch Production of Chlorobenzenes

would have been produced. The exact composition of the tars is unknown, but is assumed to be comprised chiefly of hexachlorobenzene, with <1% 1,2,4-trichlorobenzene because of extensive recycling, the presence of available chlorine in the system, and the absence of 1,2,4-trichlorobenzene in feedstock residues from various chlorination synthesis processes (EPA 1975a and EPA 1978b). Therefore, it is likely that <60 kkg of 1,2,4-trichlorobenzene were released from this process. According to the U.S. EPA (1975a), all of this tar was disposed of on land.

3.2.2 Inadvertent Sources

For the purposes of this materials balance, any process that unintentionally produces 1,2,4-trichlorobenzene and subsequently releases it to the environment is considered an inadvertent source (see Note 10, Appendix A for further details).

3.2.2.1 Production of Other Chlorinated Benzenes

The potential for the inadvertent production of 1,2,4-trichlorobenzene exists during the manufacture of other chlorinated benzenes [i.e., monochlorobenzene, 1,2- and 1,4-dichlorobenzene, the trichlorobenzenes (1,2,3- and 1,3,5-), the tetrachlorobenzenes (1,2,3,4-, 1,2,4,5- and 1,2,3,5-), pentachlorobenzene, and hexachlorobenzene]. However, only a limited amount of information was available concerning which of these manufacturing processes might actually do so.

Monochlorobenzene, 1,2- and 1,4-dichlorobenzene, and 1,2,3-trichlorobenzene are usually produced simultaneously with 1,2,4-trichlorobenzene (Lowenheim and Moran 1975, EPA 1977a). Thus the 1,2,4-trichlorobenzene inadvertenly produced and released during the manufacture of these compounds has already been accounted for in the estimate of 60 kkg generated during 1,2,4-trichlorobenzene manufacture (Section 3.2.1).

The quantity of 1,2,4-trichlorobenzene produced during 1,3,5-trichlorobenzene, tetrachlorobenzene (1,2,3,4-, 1,2,4,5-, and 1,2,3,5-) and pentachlorobenzene manufacture could not be determined from the data available but is considered to be negligible (<1 kkg each year) due to the extensive recycling of partially chlorinated benzenes during manufacture (EPA 1975b).

Most likely 1,2,4-trichlorobenzene was not released to the environment from hexachlorobenzene production in 1979 because hexachlorobenzene has not been produced for domestic consumption since 1976 (see Note 11, Appendix A for further information).

3.2.2.2 Chlorination of Water

In recent years there has been much concern about the effects of chlorination on organic materials contained in natural waters and wastewaters. Because of the current use of chlorine in water and sewage treatment procedures, the potential exists for widespread inadvertent production of chlorinated organic materials (Bellar et al. 1974). Because benzene and the dichlorobenzenes have been identified in both municipal water supplies and wastewaters, the potential role of chlorination of these waters in the inadvertent production of 1,2,4-trichlorobenzene has been investigated in several studies (EPA 1977b, EPA 1976).

Contamination of municipal drinking waters was reviewed in the National Organic Monitoring Survey (NOMS) (EPA 1977b). The study included 113 community water supplies, representing a variety of sources and treatment processes; each was sampled three times during a 12-month period (EPA 1977b). Table 3-1 shows that 1,2,4-trichlorobenzene was detected infrequently and in low concentrations. The source of the detected 1,2,4-trichlorobenzene was not readily apparent, though chlorination apparently was not a significant source.

Bellar and coworkers (1974) compared the trichlorobenzene concentration in effluent (in a sewage treatment plant) before treatment with that after treatment and found only a slight increase from 56.7 µg/l to 56.9 µg/l. Also, an EPA study (1976) showed that 1,2,4-trichlorobenzene was not detected in samples of wastewater effluent and another EPA study (1980a) stated that "...chlorination of water is not considered to be a significant source of chlorinated benzenes." Consequently, if the above studies are representative of chlorination processes for all sewage treatment plants, then it is likely that chlorination of wastewaters was not a significant inadvertent source of 1,2,4-trichlorobenzene in 1979.

3.2.2.3 Breakdown of Higher Chlorinated Benzenes

The inadvertent production of 1,2,4-trichlorobenzene via the breakdown of higher chlorinated benzenes (1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene) was also investigated. The tetrachlorobenzenes have been reported to be persistent in soil and water systems (EPA 1980b, see Note 12, Appendix A for further details). Therefore, even if the tetrachlorobenzenes are present in these media, they are not likely to release significant amounts in the 1,2,4-trichlorobenzene form. Pentachlorobenzene has also been reported to be persistent in the environment, remaining in soil for up to 3 years after application (Beck and Hansen 1974). Furthermore, because only a small quantity of pentachlorobenzene was released to the environment in 1979 (if one assumes 1977 production volumes to be similar to those for 1979), it is likely that inadvertent production of 1,2,4-trichlorobenzene via environmental degradation did not occur (see Note 13, Appendix A for further details).

Likewise, degradation of hexachlorobenzene does not appear to be an inadvertent source of 1,2,4-trichlorobenzene because: (1) it has not been domestically produced since 1976 (SRI 1980) and (2) it is a very stable, unreactive compound (EPA 1979a, see Note 14, Appendix A for further details).

Table 3-1. Occurrence of 1,2,4-Trichlorobenzene in Drinking Waters

Phase[a]	Detection Frequency[b]	Mean Concentration (μg/l)[c]	Median Concentration (μg/l)[d]
I	1/112	10	<0.4-1
II	2/113	0.29	<0.005-0.1
III	10/110	0.090	<0.005

a) In phase I, samples were collected between March and April, 1976 and stored at 2-8^{0}C for 1-2 weeks prior to analyses; for phase II, samples were collected between May and July, 1976 and allowed to stand at 20-25^{0}C for 3-6 weeks prior to analyses and; for phase III, samples were collected between November 1976 and January 1977 and were stored at 20-25^{0}C for 3-6 weeks prior to analyses.

b) Number of positive analyses/number of analyses.

c) Positive results only (samples which were above the analytical detection limits).

d) Results, from all samples (in the analyses this includes remarked data, observations noted but below analytical detection limits).

Source: EPA, 1977b; additional detail on sampling sites and locations are shown in Table 4-15.

There is a potential for the gama isomer of 1,2,3,4,5,6-hexachlorocyclohexane (lindane) to break down to 1,2,4-trichlorobenzene. Lindane has not been manufactured in the United States since 1976 and only small quantities (<500 kkg) were imported and used in pesticides in 1970. Therefore, even if lindane is degraded to 1,2,4-trichlorobenzene, it is doubtful that significant quantities of 1,2,4-trichlorobenzene were released (Nipp 1980, see Note 15, Appendix A for further details).

3.3 USES

The compound 1,2,4-trichlorobenzene was not widely used in the United States in 1979. The estimate of 7,589 kkg of the compound used in 1979 was derived from 7,301 kkg produced domestically, 886 kkg imported, and 45 kkg withdrawn from stocks minus 446 kkg, which were stockpiled and the 177 kkg that were exported (Appendix A, Note 1 for details on production, stockpiling, and imports). On the basis of use practices in 1973 and 1979, the uses are estimated as follows: 3,491 kkg in functional fluids, and 530 kkg in miscellaneous uses [degreasing agents (424 kkg), septic tank and drain cleaner formulations (53 kkg), wood preservatives (53 kkg), and abrasive formulations (<5 kkg)] (see Figure 3-1). The major user of 1,2,4-trichlorobenzene, the textile industry, released more 1,2,4-trichlorobenzene to the environment than all of the other users combined.

3.3.1 Dye Carrier

In 1979, an estimated 3,490 kkg of 1,2,4-trichlorobenzene were used by the U.S. textile industry as a dye carrier (primarily for polyester fibers). Generally, the dye, levelling agent, and carrier (1,2,4-trichlorobenzene) are applied to the material for at least 1 hour at 100°C (see Note 16, Appendix A). The material is then either rinsed and heated to 190°C for 1 minute or subjected to an alkaline scour at 70-80°C with a sulfated fatty alcohol to remove the carrier (Lewis 1975, EPA 1977a and 1980a).

Most of the 1,2,4-trichlorobenzene, in the form of spent dye carrier, is discharged to water where it may or may not be removed by wastewater treatment practices. The amount of 1,2,4-trichlorobenzene possibly retained by the material or emitted to the atmosphere during dyeing operations is unknown. The U.S. EPA (1980a) estimated that 3% of the amount used might be absorbed by the fiber, 1% would be released to the air, while 96% would be discharged to water. However, because these figures are not substantiated, a worst case scenario is used in this report, i.e., that all of the 1,2,4-trichlorobenzene used in the textile industry (3,490 kkg) was released to the environment (see Table 3-2).

The quantities of 1,2,4-trichlorobenzene released to the environment from domestic wet-processing textile mills in 1979 are estimated in Table 3-2 (see Appendix A, Note 17 and Appendix B, Table B-1 for

Table 3-2. Estimated Quantities of 1,2,4-Trichlorobenzene-Containing Wastes Released to the Environment from Textile Operations in 1979[a]

Operation	Environmental Releases (kkg) Water[b] D	I	Land[c]	Air[c]	Total
Wool Scouring	21	50	17	17	105
Woven Fabric Finishing[d]	235	913	184	169	1,501
Knit Fabric Finishing	283	1,225	207	169	1,885
Total	539	2,188	408	355	3,490

a) See Appendix A, Note 17 and Appendix B, Table B-1 for further details.
b) D=quantity of 1,2,4-trichlorobenzene discharged directly to surface waters and I=quantity of 1,2,4-trichlorobenzene indirectly discharged to publicly owned treatment works.
c) Based on the assumption that the 1,2,4-trichlorobenzene removed during wastewater treatment was sent to land when advanced treatment was used, and when biological treatment practices (or equivalent) were used the wastes were equally divided between air and land.
d) Includes simple processing and complex processing plus desizing.

Source: EPA, 1979b; see Table B-2, Appendix B.

further details). Most (2,727 kkg, or 78%) of these wastes was discharged to water, with 539 and 2,188 kkg discharged to surface waters and POTWs, respectively. As shown in Table 3-2 and B-1, the remaining 1,2,4-trichlorobenzene originally contained within the wastewaters was most likely removed by the treatment facilities at the textile mills and disposed of on land (408 kkg) and/or emitted to the atmosphere (355 kkg).

3.3.2 Pesticide Production

Nearly 2,200 kkg of 1,2,4-trichlorobenzene were consumed by the U.S. pesticide industry in 1979 (Figure 3-1). The compound was used as an intermediate during the production of three pesticides: dicamba (herbicide), stirofos (insecticide), and trichlorodinitrobenzene (fungicide) (see Appendix A, Note 18 for chemical names and Note 19 for process descriptions, Sittig 1977). Production statistics for these pesticides were not reported by the producers because of the confidentiality of the information (see Appendix A, Note 20 for further details, SRI 1980). Therefore, it is assumed that 33% (or 733 kkg) of the total quantity of 1,2,4-trichlorobenzene used by the pesticide industry (2,200 kkg) was consumed/converted during the production of each pesticide. Furthermore, based on process descriptions, approximately 1% (or 22 kkg) of the total 1,2,4-trichlorobenzene used in the production of the aforementioned pesticides was assumed to be released to the environment, of which, two-thirds was emitted to the atmosphere and one-third was discharged to POTWs (Figure 3-1, Richter 1961, Phillips and Word 1963, Dittmar 1956, and Sittig 1977).

In the first step of dicamba manufacture, 90% of the 1,2,4-trichlorobenzene used (or 90% of 733 = 660 kkg) is converted to 2,4-dichlorophenol (Sittig 1977, see Appendix A, Note 19 for details). Therefore, not more than 73 kkg of 1,2,4-trichlorobenzene could have been released to the environment. However process descriptions indicate that most of this 1,2,4-trichlorobenzene was probably converted into other compounds during side reactions so that <1% (or 7 kkg) of that used for dicamba manufacture was released to the atmosphere from fugitive emissions and handling (Sittig 1977, Richter 1961).

In the manufacture of stirofos, 1,2,4-trichlorobenzene was incorporated into the end product with 77% efficiency (Sittig 1977, Phillips and Word 1963, see Appendix A, Note 19 for details). Thus, 23% (or 169 kkg) of the total 1,2,4-trichlorobenzene used in stirofos formulation (733 kkg) could have been released to the environment. However, most of this 1,2,4-trichlorobenzene was probably converted into other compounds during side reactions; and if recycling is taken into account, probably <1% (or 7 kkg) of the total 1,2,4-trichlorobenzene used was released to the atmosphere from handling and fugitive emissions (Phillips and Word 1963, Sittig 1977).

According to Sittig (1977) and Dittmar (1956), 91% of the 1,2,4-trichlorobenzene used as feedstock for trichlorodinitrobenzene formulation was consumed. Therefore, 9% (or 70 kkg) of the original amount of 1,2,4-trichlorobenzene (733 kkg) could have been released to the environment. However, the process description indicates that most of this was converted into other compounds during side reactions, so that <1% (or 7 kkg) of the total 1,2,4-trichlorobenzene used was discharged to water (see Appendix A, Note 19 for further details).

3.3.3 Functional Fluids

In 1979, 1,370 kkg of 1,2,4-trichlorobenzene were used in functional fluids such as dielectric liquids and transformer oils. Liquid dielectric compositions containing 1,2,4-trichlorobenzene (0.3-20% by weight) are primarily used in electrical apparatus such as capacitors and transformers (Lapp and Sadler 1976, see Note 21, Appendix A for further details).

During the manufacture of electrical apparatus impregnated with 1,2,4-trichlorobenzene-containing dielectric liquids, little 1,2,4-trichlorobenzene was probably released to the environment. The liquid dielectric was introduced into the hermetically sealed apparatus through small seal holes in the casings. It is assumed that <1% (or 14 kkg) of the total 1,2,4-trichlorobenzene impregnated into such apparatus (1,370 kkg) was released, with 7 kkg of the total discharged to water during cleaning and 7 kkg emitted to air as fugitive emissions (Lapp and Sadler 1976).

The remaining 1,2,4-trichlorobenzene used in functional fluids in 1979 (i.e., 99% or 1,356) was contained within the apparatus, isolated from the environment. However, these capacitors and transformers periodically rupture, leak and/or become obsolete and must be discarded. If the quantity of 1,2,4-trichlorobenzene incorporated into electrical apparatus in 1979 is assumed to be equal to the amount released that year by the disposal of apparatus manufactured prior to 1979, then 1,356 kkg would have been lost to the environment. Furthermore, it is assumed that all of this 1,2,4-trichlorobenzene is disposed of on land.

3.3.4 Miscellaneous Uses

The miscellaneous uses of 1,2,4-trichlorobenzene comprised only 7% of the total quantity of 1,2,4-trichlorobenzene domestically consumed in 1979 and totalled about 530 kkg (Figure 3-1). These uses include: degreasing agents (424 kkg), septic tank and drain cleaner formulations (53 kkg) wood preservatives (53 kkg), and abrasive formulations (<5 kkg).

3.3.4.1 Degreasing Agents

An estimated 424 kkg of 1,2,4-trichlorobenzene were used in degreasing agents in 1979, of which, 382 kkg were used for stripping electronic wafers (see Notes 6 and 22, Appendix A for details). Based on EPA emission rates and waste solvent recovery values, an estimated total of 286 kkg of 1,2,4-trichlorobenzene were released to the environment from wafer stripping as follows: 190 kkg were emitted to the atmosphere, 67 kkg disposed of on land and 29 kkg discharged to POTWS (see Table 3-3 for details).

Table 3-3. Estimated Quantities of 1,2,4-Trichlorobenzene in Metric Tons (kkg) Released to the Environment During Electronic Wafer Degreasing Operations[a]

Quantity Consumed	Quantity Recycled	Estimated Environmental Releases			
		Water		Land	Air[b]
		Surface	POTW		
382	86		29	67	190

a) Approximately 50% (191 kkg) of the total quantity consumed (382 kkg) becomes contaminated with inpurities during operation where 45% (86 kkg), 35% (67 kkg), 15% (29 kkg) and 5% (10 kkg) of this waste solvent is reclaimed and recycled, disposed to landfill and plant grounds, discharged to POTWs, and destroyed by incineration, respectively; the remaining 50% (191 kkg) is emitted to the atmosphere (see footnote b); numbers may not add due to rounding.

b) Based on 430 g solvent emitted per kilogram of solvent consumed (±30% with an average of 164 kkg) it is assumed all of the 1,2,4-trichlorobenzene carried out by the parts during processing (26 kkg) is emitted to air.

Source: EPA, 1979c.

Approximately 42 kkg of 1,2,4-trichlorobenzene were incorporated into a degreasing agent formulation used to clean automotive engines (see Appendix A, Note 6 for calculations). Losses of this isomer were most likely to the atmosphere and probably can be attributed to evaporation of the cleaning compound during mixing and handling. Therefore all of the 1,2,4-trichlorobenzene contained in formulations used to clean automotive engines (42 kkg) was assumed to be emitted to the atmosphere (Figure 3-1).

3.3.4.2 Septic Tank and Drain Cleaners

In 1979, 53 kkg of 1,2,4-trichlorobenzene were used in septic tank and drain cleaners (Figure 3-1, Hull and Co. 1980, see Appendix A, Note 6 for calculations). If one assumes that one-half of the 1,2,4-trichlorobenzene used in these products was contained in septic tank cleaners and one-half was contained in drain cleaners, then 27 kkg of 1,2,4-trichlorobenzene were disposed of on land and 27 kkg were discharged to municipal waters as these products were used.

3.3.4.3 Wood Preservatives

In 1979, 53 kkg of 1,2,4-trichlorobenzene were used in a special formulation used to preserve wood (see Appendix A, Note 6 for calculations). According to Hull (1980), this formulation is injected into standing wood buildings to preserve the wood and can act as an insecticide. If 1% of the 1,2,4-trichlorobenzene is lost to the atmosphere during mixing, handling, and injection, then <1 kkg would have been emitted to air, while the remaining 52 kkg would have been retained in the wood.

3.3.4.4 Abrasive Formulations

A minor application of 1,2,4-trichlorobenzene, probably accounting for <5 kkg in 1979, is its use as a wetting and bonding agent in the manufacture of abrasive grinding wheels (Richards 1980, Hull and Co. 1980, see Appendix A, Note 6 for calculations and Note 23 for manufacturing details). Most of the 1,2,4-trichlorobenzene vaporizes during wheel curing operations so that less than 0.3% by weight of the grinding wheel is 1,2,4-trichlorobenzene and grinding wheel use would not release significant amounts of the compound (Richards 1980, Hull and Co. 1980). Thus, nearly all of the 1,2,4-trichlorobenzene used in grinding wheel manufacture, (<5 kkg) is emitted to the atmosphere during formulation, mixing, and curing (Richards 1980).

3.4 MUNICIPAL DISPOSAL OF 1,2,4-TRICHLOROBENZENE

This section deals with the ultimate disposal of 1,2,4-trichlorobenzene to municipal waste facilities. These include: publicly-owned treatment works (POTWs) and urban refuse disposal.

3.4.1 POTWs

Input of 1,2,4-trichlorobenzene to POTWs is largely dependent upon variations in industrial discharges feeding the POTWs and the types of industry in the particular municipal area.

An overall materials balance for 1,2,4-trichlorobenzene in POTWs, presented in Table 3-4, can be constructed using a total POTW flow of approximately 10^{11} l/day and a mean concentration of <1 µg/l in influent and <2 µg/l in effluent (EPA 1979d, 1980c). If influent and effluent flow rates are assumed to be equal (i.e., water loss from sludge removal and evaporation are small compared with influent flows), then 73 kkg of 1,2,4-trichlorobenzene would have been discharged from POTWs. However, because significantly larger quantities of 1,2,4-trichlorobenzene are known to have been released from the textile industry alone, the discharges of 1,2,4-trichlorobenzene from POTWs could be considerably higher (Garrison and Hill 1972, Simmons *et al.* 1977, EPA 1980b).

The quantity of 1,2,4-trichlorobenzene discharged in sludge can be estimated from the concentration in sludge and the quantity of dry sludge produced annually [5.5×10^6 kkg (EPA 1980 c)]. If the average 1,2,4-trichlorobenzene concentration of wet sludge is assumed to be 25 µg/l (see Table 3-4), wet sludge is assumed to be 95% water by weight, and 1 liter of sludge is assumed to weigh 1 kg, approximately 3 kkg of 1,2,4-trichlorobenzene were discharged as sludge (which was probably disposed of on land).

3.4.2 Urban Refuse

Urban refuse is handled by three methods: (1) energy recovery (primarily by incineration), (2) material recovery and (3) disposal through incineration or landfills. Urban refuse can be divided into two major components: a combustible fraction (e.g., papers, plastics, fabrics, etc.) and a noncombustible fraction (e.g., ferrous and nonferrous metals, glass, ceramics, etc.). Although specific data concerning the release of 1,2,4-trichlorobenzene from municipal incinerators could not be found, incineration of chlorotoluene- and chlorobenzene-containing wastes results in a destruction efficiency of greater than 99.9% (MacDonald *et al.* 1977). Therefore, it is most likely that 1,2,4-trichlorobenzene-containing wastes, once combusted, are likewise not a significant source of 1,2,4-trichlorobenzene releases to the environment.

Nearly 1,360 kkg of 1,2,4-trichlorobenzene are assumed to have been contained in dielectric liquids within electrical apparatus disposed of in urban refuse. It is assumed that the amount of 1,2,4-trichlorobenzene consumed annually in dielectric fluids equals the amount contained in equipment discarded annually; these fluids are then released to land as a result of corrosion and rupture. On the basis of these assumptions, 1360 kkg of 1,2,4-trichlorobenzene are released from this source each year.

Table 3-4. 1,2,4-Trichlorobenzene Distribution in POTW Influent, Effluent and Sludge Samples from Select Urban Sites

Plant Number	% Industrial Contribution	Average Flow[a] (l/day)	Concentrations (μg/l)[b] Influent	Effluent	Combined Sludge
1	30	3970	0	<10	<10
2	<5	340			
3	10	390	< 10	<10	23
4	7	3120			
5	10	980			
6	38	260			
7	15	1890			
8	10	850			
9	10	1800			
10	5	1140	1	<5	
11	18	1550			
12	50	1480			
13	33	640			
14	25	510			
15	25	190			
16	16	5300			
17	25	370			
18	50	3100			
19	20	2650	<5	<5	272[c]
20	15-22	3790	14	<5	158[c]

a) Historical flowrate; percentage of flow contributed by industrial sources ranges from <1-35%.
b) Blank entry indicates that 1,2,4-trichlorobenzene was not detected.
c) Average concentration of 1,2,4-trichlorobenzene in primary and secondary sludge.

Source: EPA, 1980c.

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4.0 FATE AND DISTRIBUTION IN THE ENVIRONMENT

4.1 INTRODUCTION

This chapter identifies the environmental pathways of 1,2,4-trichlorobenzene resulting from its release into the environment. Four major sources of release of the chemical in 1979 identified in Chapter 3.0 are illustrated in Figure 4-1. The textiles industry, utilizing 1,2,4-trichlorobenzene as a dye carrier, is the largest consumer and largest source of release of the chemical. Most of the releases from the textile industry are to publicly owned treatment works (POTWs). This industry is the only identified direct discharger of 1,2,4-trichlorobenzene to surface water, and releases 1,2,4-trichlorobenzene to air and land as well. Other significant sources of 1,2,4-trichlorobenzene release to the environment include the disposal of used electrical apparatus; primary 1,2,4-trichlorobenzene production; and production of pesticides, herbicides and functional fluids.

The remainder of this chapter describes the fate of 1,2,4-trichlorobenzene following its release to the environment as it is transformed or transported in environmental media. The fate of 1,2,4-trichlorobenzene in the aquatic environment is discussed in Section 4.3. The ultimate fate of the chemical in ambient surface waters and drinking waters is identified and quantified to the degree possible. Output from the EXAMS model is used to support and amplify laboratory studies regarding the aquatic fate of 1,2,4-trichlorobenzene. Section 4.4 discusses atmospheric fate. Only 12% of all identified environmental releases of 1,2,4-trichlorobenzene are to the air and the compound is not believed to persist as a result of photodegradation or wet and dry deposition. Terrestrial fate is discussed in Section 4.5, including possible sinks for 1,2,4-trichlorobenzene deposited on land, such as groundwater, accumulation by microbial organisms, and soil particles (through adsorbtion). Finally, the fate of 1,2,4-trichlorobenzene in treated waters is explored in Section 4.6. Of particular concern here are the efficiencies of POTWs, the likelihood of formation of 1,2,4-trichlorobenzene from chlorination of waste and drinking waters, and occurrence of 1,2,4-trichlorobenzene.

Throughout this chapter, the available data for laboratory and field studies are discussed as appropriate. Where they are available, monitoring data are presented to provide an accurate picture of actual environmental conditions to which humans and other receptors may be exposed.

4.2 PHYSICOCHEMICAL PROPERTIES

Table 4-1 lists physical and chemical properties for 1,2,4-trichlorobenzene. Three trichlorobenzene isomers (1,3,5-; 1,2,3-; 1,2,4-) are commercially produced in the U.S. During the chlorination of benzene, orientation effects direct the chlorines to attach to certain positions on the benzene ring such that 1,2,4-trichlorobenzene is the predominant trichlorobenzene isomer formed (ca. 85-90%). Some commercial mixtures

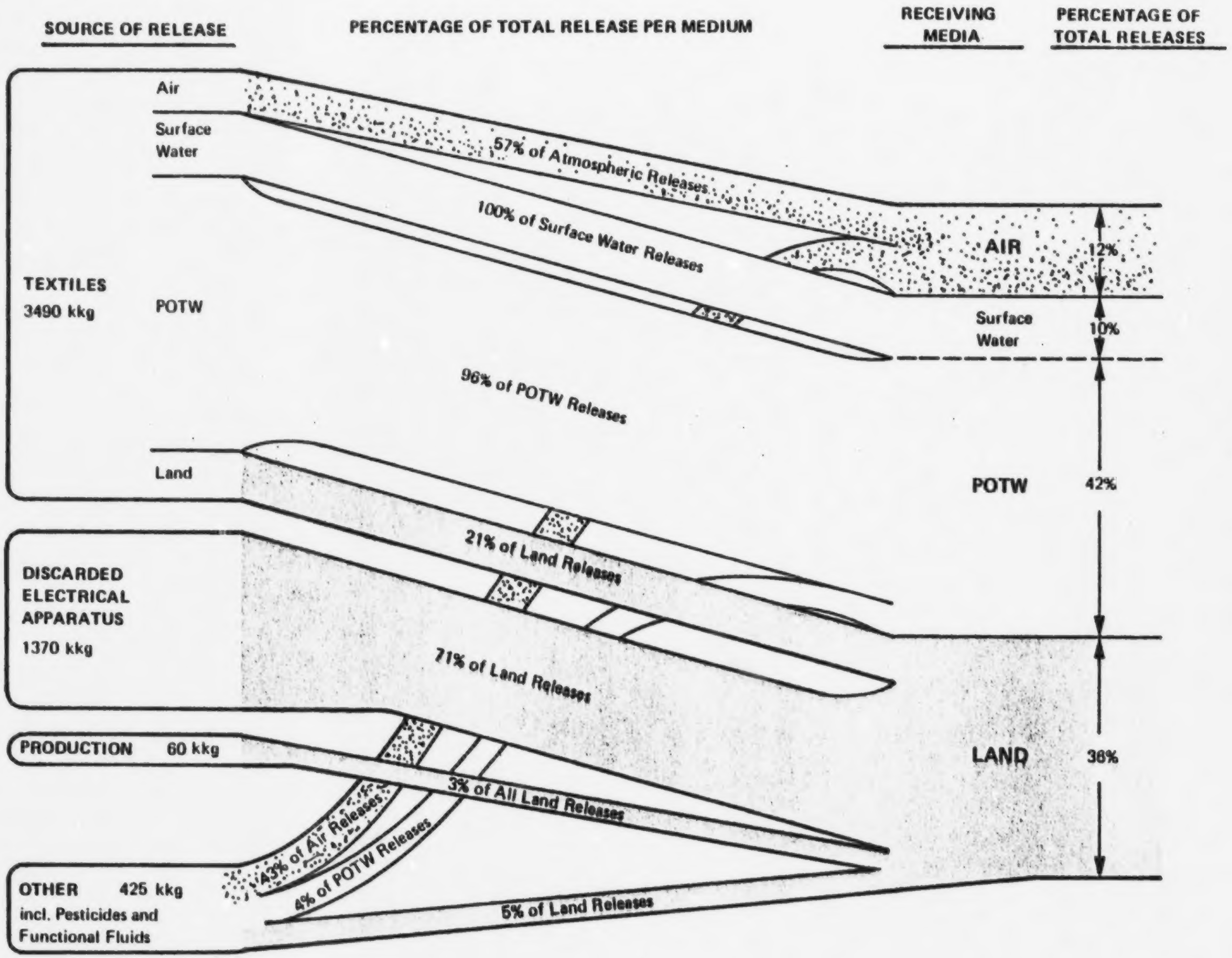
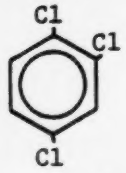

SOURCE OF RELEASE
PERCENTAGE OF TOTAL RELEASE PER MEDIUM
RECEIVING MEDIA
PERCENTAGE OF TOTAL RELEASES
TEXTILES
3490 kkg
Air
Surface Water
POTW
Land
57% of Atmospheric Releases
100% of Surface Water Releases
96% of POTW Releases
21% of Land Releases
DISCARDED ELECTRICAL APPARATUS
1370 kkg
71% of Land Releases
PRODUCTION 60 kkg
3% of All Land Releases
OTHER 425 kkg
incl. Pesticides and Functional Fluids
43% of Air Releases
4% of POTW Releases
5% of Land Releases
AIR
12%
Surface Water
10%
POTW
42%
LAND
38%

FIGURE 4-1 ENVIRONMENTAL RELEASES OF 1,2,4-TRICHLOROBENZENE

Source: Arthur D. Little, Inc.

TABLE 4-1. PHYSICAL AND CHEMICAL PROPERTIES OF 1,2,4-TRICHLOROBENZENE

Molecular Weight:	18.45
Structure:	
Melting Point:	16.95°C (62.5°F)
Boiling Point:	213.5°C (416.3°F)
Water Solubility:	30 mg/l (at 25°C)
Specific Gravity at 25/25°C:	1.454
Log Octanol/Water Partition Coefficient:	4.27
Vapor Pressure at 25°C:	0.42 mm Hg (torr.)

Source: Morrison and Boyd (1978).

sold as "trichlorobenzene" are known to contain approximately 85% 1,2,4-trichlorobenzene; the other isomers are present in the proportions in which they occur during production (Hardie 1964, Morrison and Boyd 1973). The chemical and physical behavior of the three isomers is very similar. Trichlorobenzene is a very stable organic molecule, because the halogenation of benzene deactivates the ring to electrophilic substitution. Aryl halides are also highly unreactive to nucleophilic substitution (Morrison and Boyd 1973). Thus chemical degradation not mediated by biological processes is not likely to be an important fate pathway for 1,2,4-trichlorobenzene.

4.3 AQUATIC FATE

4.3.1 Introduction

As discussed in Chapter 3.0, releases to surface water are a major point of entry into the environment for 1,2,4-trichlorobenzene. The single most important use of 1,2,4-trichlorobenzene is in the dyeing and textile industry. The 1,2,4- isomer of trichlorobenzene has been found in the effluent wastewaters of these industries at concentrations ranging from 0.1 μg/l to 1 mg/l (Hites 1973, Gaffrey 1976 and 1977).

From 25% to 30% of the 1,2,4-trichlorobenzene produced is used in insecticide and herbicide preparations. Some is used in aquatic herbicides; that used in other insecticides/herbicides is likely to contaminate runoff. These combined contributions would result in an occurrence of 1,2,4-trichlorobenzene in surface water that is not associated with industrial activity.

This section characterizes the fate processes that transform or transport 1,2,4-trichlorobenzene in surface water and determine the ultimate distribution in the environment. Monitoring data are analyzed to determine the levels of 1,2,4-trichlorobenzene in effluents associated with municipal wastewater systems, and the textile and other industries with 1,2,4-trichlorobenzene contaminated wastes. The fate processes associated with 1,2,4-trichlorobenzene in water are identified and discussed theoretically and on the basis of EXAMS modeling results. Concentrations of 1,2,4-trichlorobenzene detected in ambient waters and aquatic organisms are reported.

4.3.2 Concentrations in Effluents to Surface Waters

Concentrations of 1,2,4-trichlorobenzene in industrial effluents discharged to surface water are reported in the STORET Water Quality System maintained by the U.S. EPA (U.S. EPA 1980a). All concentrations currently recorded in STORET are remarked data, that is, are below established detection limits but are above zero. There were 588 observations throughout the U.S. as shown in Table 4-2. These were frequently low, with 72% indicating concentrations belwo 10 μg/l. Approximately 28% of the observed concentrations were between 10 μg/l and 100 μg/l, with the highest concentrations in the Ohio River and Upper Mississippi River basins. There was only one observation greater than 1000 μg/l

TABLE 4-2. DISTRIBUTION OF REMARKED EFFLUENT 1,2,4-TRICHLOROBENZENE CONCENTRATIONS FOR MAJOR RIVER BASINS IN THE UNITED STATES--STORET, 1980

		Concentrations (μg/1)			
Major River Basin	Number of Observations	≤10.0	10.1-100	100.1-999.9	≥1000
Northeast	147	118	20		
North Atlantic	72	72			
Southeast	97	95	1		1
Tennessee River	18	18			
Ohio River	76	17	59		
Lake Erie	6	6			
Upper Mississippi	71	8	63		
Lake Michigan	1	1			
Missouri River	26	17	9		
Lower Mississippi	11	11			
Colorado River	5	4	1		
Western Gulf	7	7			
Pacific Northwest	39	38	1		
California	9	8	1		
Great Basin	1	1			
Puerto Rico					
Virgin Islands	1	1			
Lake Superior	1	1			
Unlabelled					
UNITED STATES	588	423	164		1

Source: STORET Water Quality Control Information System, retreived on October 28, 1980.

Note: Remarked are all values between 0 and the detection limits.

and this was reported for the Southeast River basin (U.S. EPA 1980a). The mean recorded effluent observation is 12 µg/l and the maximum is 2500 µg/l.

Concentrations of 1,2,4-trichlorobenzene in municipal wastewater, industrial and urban runoff effluents were reported at several locations in the U.S. during different seasons of the year as shown in Table 4-3 and Table 4-4. These ranged from less than 0.01 µg/l in the fall to 275 µg/l in the summer. One industrial discharge sampled in the spring in Chattanooga, Tennessee contained 500 µg/l 1,2,4-trichlorobenzene. Generally, where summer and fall values were reported for the same site, the levels of 1,2,4-trichlorobenzene were twice to 20 times as high in the summer as in the fall.

In recent sampling of industrial effluents, 1,2,4-trichlorobenzene was detected in effluents from the textile industry, steam electric power plants, and the non-ferrous metals industry (U.S. EPA 1980d). As shown in Table 4-5, these concentrations range from means of 1 µg/l to 410 µg/l and maxima of 260 µg/l to 2700 µg/l for raw wastewater. Treated waste effluents range from 4.4 µg/l to 610 µg/l on the average to maxima of 47 µg/l to 1500 µg/l.

It is clear from these data that levels of 1,2,4-trichlorobenzene were well above ambient levels at isolated discharge points associated with industries producing (intentionally or inadvertently) or using 1,2,4-trichlorobenzene.

4.3.3. Fate Processes

4.3.3.1 Volatilization

Mathematical models and laboratory studies have shown that a significant fraction of the 1,2,4-trichlorobenzene released to surface water may be volatilized to the atmosphere in a matter of hours (Mackay and Leinonen 1975, Garrison and Hill 1972). Other authors have suggested that suspended microbiota can reduce the rate of volatilization (Garrison and Hill 1972).

Several mathematical models have been developed for estimating the rate of volatilization of organic pollutants from surface waters. These models typically treat such volatilization as a first-order process. The volatilization rates produced by each of the various models correlate fairly well with the experimentally observed rates (Appendix C). A common approach was developed (Appendix C) to compute volatilization rates. Parameters such as the wind velocity, the water current velocity, the depth of the water body, and the molecular weight of the chemical of interest are used with the Henry's Law constant (the ratio of vapor pressure to water solubility) to calculate an overall mass-transfer coefficient. From this, the volatilization rate constant and half-life for volatilization can be calculated.

TABLE 4-3. SEASONAL LEVELS OF 1,2,4-TRICHLOROBENZENE IN SELECTED EFFLUENT WATERS

Location	Source	Seasonal Mean Detected (μg/1)			
		Summer	Fall	Winter	Spring
Catawba Creek, NC	Industrial discharge	12	–[a]	–	–
Chattanooga Creek, TN	Industrial discharge	–	–	–	500
Joint Water Pollution Control Plant (JWPCP)	Municipal wastewater	6.0	1.8	–	–
Hyperion Sewage Treatment Works, LA (HSTW)	5-mile effluent, municipal wastewater	6.7	3.1	–	–
HSTW, LA	7-mile effluent, municipal wastewater	275	130	–	–
Orange County Sewage Department, CA (OCSD)	Municipal wastewater	0.30	–	–	–
Port Loma Sewage Treatment Plant, CA (PLSTP)	Municipal wastewater	0.23	<0.01	–	–
Oxnard, CA Sewage Treatment Plant (OSTP)	Municipal wastewater	0.9	0.25	–	–

Source: U.S. EPA (1980b).

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[a] – indicates that no samples were taken.

TABLE 4-4. OBSERVATIONS OF 1,2,4-TRICHLOROBENZENE LEVELS IN WASTEWATERS

Source/Location	Concentration (μg/1)	References
Delaware River at Philadelphia, PA:		Sheldon and Hites (1979)
Effluent, unidentified chemical plant A	200	
Treatment plant influent incl. A	20	
Treatment plant effluent to river	10	
2-4 miles upstream of treatment plant discharge	"trace"	
Influent to a municipal wastewater treatment plant adjacent to the Ohio River (no date)	66.9	Bellar *et al.* (1974)

TABLE 4-5. CONCENTRATIONS OF 1,2,4-TRICHLOROBENZENE IN WASTE STREAMS OF INDUSTRIAL SOURCES TO WATER

	Concentrations (μg/1)		
Source	Minimum	Maximum	Mean
Raw Waste Streams			
Textile Mills	n.a.	2700	410
Steam Electric Plants	n.a.	n.a	10
Foundries	n.d.	n.a	7
Non-Ferrous Metals	n.d.	260	22
Treated Waste Streams			
Textile Mills	n.a.	1500	610
Foundries	<20.0	570	290
Non-Ferrous Metals	n.d.	47	4.4

Note: n.a.: not available
n.d.: not detected

Source: U.S. EPA (1980d)

For a hypothetical unpolluted stream 1 m deep, moving at 6 m per second, with a wind speed of 5 m per second (fairly typical conditions), the half-life for volatilization of 1,2,4-trichlorobenzene calculated by this model is 5.8 hours. Since about 95% of the "resistance" to volatilization is in the liquid phase (Mackay and Leinonen 1975), parameters such as stream depth and stream flow velocity greatly affect the rate of volatilization.

Laboratory studies suggest that volatilization rates are similar although slightly more rapid than those determined from mathematical models. Ninety percent of the 1,2,4-trichlorobenzene volatilized in less than 4 hours from an aerated, distilled water sample originally containing 100 mg/l of 1,2,4-trichlorobenzene. This corresponds to a volatilization half-life of about 0.5 hour (Garrison and Hill 1972). The volatilization half-life increases to about 7.2 hours when the distilled water sample is not aerated.

The latter observation suggests that under conditions most favorable to volatilization, 1,2,4-trichlorobenzene may be volatilized quickly due to its short half-life of 1 hour or less. Under quiescent conditions, the volatilization half-life process decreases considerably, on the order of several hours.

The presence of organic sediment and biomass is expected to decrease the rate of volatilization. The relatively large octanol/water partition coefficient (4.26) for 1,2,4-trichlorobenzene indicates that the chemical will partition into the lipid (fat-containing) fractions of biota. Absorbtion by biota removes 1,2,4-trichlorobenzene from the body of water and hence the quantity available for volatilization decreases. When a sample with an initial concentration of 50 mg/l of 1,2,4-trichlorobenzene and "mixed cultures of aerobic microorganisms" was aerated, although 90% of the concentration was lost by 24 hours, low levels of the chemical persisted for up to 9 days (Garrison and Hill 1972). When this is compared with the 0.5 hour half-life for complete volatilization from aerated distilled water containing only the 1,2,4-trichlorobenzene, it becomes clear that although volatilization must still be considered an important environmental pathway for 1,2,4-trichlorobenzene, the presence of microorganisms reduces volatilization apparently by biodegradation and/or absorption. No information was given on the experimental procedures to determine whether the two studies are directly comparable. Additionally, the presence of other absorbing material, i.e., organic matter, was not measured to determine its role in adsorption of the chemical.

4.3.3.2 Bioaccumulation

Trichlorobenzene is known to bioaccumulate in fish tissue. Laboratory studies indicate a rapid initial build-up in tissue. Rainbow trout had a bioconcentration factor of 100 above water levels at 8 hours and 400 at 4 days in muscle tissue. Partial biotransformation of the compound occurred in the fish as indicated by transformation products in the muscle and liver (Melancon et al. 1979). In field studies, however, tissue levels of sampled fish are generally low, on the order of 10 µg/kg or less (Young and Heesen 1977, Ofstad et al. 1978). The bioconcentration factor for these levels is difficult to calculate from field studies because the level and duration of exposure are unknown. Therefore, it is not possible to compare these results to laboratory results.

In the STORET Water Quality System, 1,2,4-trichlorobenzene concentrations were not detected in 72 samples of fish tissue taken from various water types in western states, Texas, and Louisiana (U.S. EPA 1980a).

4.3.3.3 Absorption by Biota

Absorption of 1,2,4-trichlorobenzene by waterborne biota appears to be one removal mechanism for the 1,2,4-trichlorobenzene released to surface water that is not volatilized, though the available studies did not indicate the exact breakdown of the two removal processes.

Lu and Metcalf (1975) found that the ecological magnification of certain benzene derivatives correlated well with both their water solubility and their octanol/water partition coefficient. Although the 1,2,4-isomer was not studied by these authors, both monochlorobenzene and hexachlorobenzene were studied. Based on their model, the ecological magnification of 1,2,4-trichlorobenzene would be within the range of 1100 to 2500 in fish. Lu and Metcalf performed their studies on the basis of the dry weight of the organism. Macek et al. 1977, observed bioconcentration factors of 142 and 182 for daphnids and fish, respectively. The difference between the values given in these two studies may be due to a difference in the method of determining the concentration of the chemical in the organisms. Other studies indicate non-quantitatively that 1,2,4-trichlorobenzene is absorbed by biota (Marinucci and Barth 1979, Callahan et al. 1979).

4.3.3.4 Adsorption onto Sediment

Little information was found on the extent to which 1,2,4-trichlorobenzene is adsorbed by sediment. When used with a soil adsorption coefficient of 11,000 (Fiksel and Segal 1980), a soil organic carbon content of 2%, and assuming that adsorption onto sediment is comparable to that of soil, and a concentration of 1,2,4-trichlorobenzene of 0.1 mg per liter (kilogram) in the water above the sediment, the Freundlich equation yields a value of 22 mg of 1,2,4-trichlorobenzene adsorbed per kilogram of sediment.

Sediment, both suspended and settled, may adsorb 1,2,4-trichlorobenzene from solution, but the magnitude of adsorption will be dependent upon the organic fraction of the sediment and also on absorption by biota.

[The EXAMS and other computer model results best define how 1,2,4-trichlorobenzene partitions between these media (see Section 4.3.4).] That which is adsorbed by sediment is expected to be slowly degraded by the microorganisms associated with particulates or, in the case of the anaerobic layer of bottom sediment, may persist for longer periods of time.

4.3.3.5 Chemical Degradation

Processes such as hydrolysis, photolysis, and oxidation are not likely to occur to any significant extent for 1,2,4-trichlorobenzene in surface water. As mentioned earlier, the trichlorobenzene molecule is inherently stable in all types of chemical reactions. It is unlikely that 1,2,4-trichlorobenzene will hydrolyze in ambient water due to the extreme difficulty with which aryl halides undergo nucleophilic substitution. Although no specific data were readily available on the oxidation of 1,2,4-trichlorobenzene, the compound is reportedly susceptible to attack by hydroxyl radicals in the atmosphere (Callahan *et al*. 1979). Although the high energy of ambient ultraviolet radiation can degrade the trichlorobenzene molecule, such photolysis has been shown not to occur with 1,2,4-trichlorobenzene in water (Akermak 1978).

4.3.4 Modeling of Environmental Distribution

For the purpose of estimating the potential fate of 1,2,4-trichlorobenzene in various generalized aquatic environments under conditions of continuous discharge, the EXAMS (Exposure Assessment Modeling System) model AETOX 1 was implemented (U.S. EPA 1980c). The physical-chemical properties and reaction rate constants used as input parameters are listed in Table 4-6. An arbitrary loading rate of 1.0 kg/hr was chosen as realistic under occasional circumstances in the environment and used to compare the compound's fate in different aquatic systems: a pond, oligotrophic lake, eutrophic lake, average river, turbid river, and coastal plain river. The simulated systems represent "average" U.S. water bodies. Their characteristics (i.e., biomass, sediment concentrations, climatic conditions) are described in the model output (U.S. EPA 1980c) but only flow, length, and depth are given in Table 4-7 for the purposes of brevity.

Tables 4-8 and 4-9 present the output of the EXAMS simulations by ecosystem type. Presented are average concentrations at equilibrium in various media (water, sediment, biota, etc.) and percent loss due to different fate processes.

According to the EXAMS results, the most significant removal process for trichlorobenzene was volatilization. In the low-flow, physically static systems -- the pond and lakes -- volatilization accounted for more than 90% of the chemical's loss, resulting in a system clearance time (assuming cessation of discharge after equilibrium is attained) of 6.5 to 19 months. The lower amount of sediment and biomass in the oligotrophic as

TABLE 4-6. PARAMETERS FOR 1,2,4-TRICHLOROBENZENE USED IN EXAMS ANALYSIS

Property	Value[a]
Molecular Weight	181.45 g/mole
Solubility	30 mg/1
Liquid Phase Transport Resistance	0.456
Henry's Law Coefficient	2.31×10^{-3} m^3 atm/mole
Vapor Pressure	0.29 torr
Partition Coefficient:	
• Biomass/Water	$3070\ \frac{\mu g/g}{mg/1}$
• Sediment/Water	$1.02\times10^{4}\ \frac{mg/kg}{mg/1}$
• Octanol/Water	$1.86\times10^{4}\ \frac{mg/1}{mg/1}$
Chemical Oxidation Rate	
• Water	1 mole/1/hr
• Sediment	360 mole/1/hr
Biodegradation Rate	
• Water	1×10^{-10} mole/1/hr
• Sediment	1×10^{-10} mole/1/hr

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[a] All data from SRI (1980).

TABLE 4-7. FLOW AND DEPTH OF EXAMS SIMULATED SYSTEMS[a]

		Depth (m)			
System	Water Flow (m^3/day)	Water Column	Sediment	Sediment Mass in Water Column (kg)	Length (m)
Pond	0.643	2	0.05	600	NA
Eutrophic Lake	$4.1x10^5$ (b)	20 (c)	0.05	2695 (c)	NA
Oligotrophic Lake	$4.1x10^5$ (b)	20 (c)	0.05	525 (c)	NA
River	$2.4x10^7$	3	0.05	$6x10^4$	3
Turbid River	$2.4x10^7$	3	0.05	$3x10^5$	3
Coastal Plain River	$2.4x10^6$	3	0.05	6000	3

---

[a] All data from U.S. EPA (1980c) output.

[b] Average flow for littoral zone, epilimnion and hypolimnion.

[c] Includes epilimnion and hypolimnion (deepest part of lake).

TABLE 4-8. STEADY-STATE CONCENTRATIONS IN VARIOUS GENERALIZED AQUATIC SYSTEMS RESULTING FROM CONTINUOUS 1,2,4-TRICHLOROBENZENE DISCHARGE AT 1.0 kg/hr[a]

		Maximum Concentrations						
System	Loading	Water Dissolved (mg/1)	Water Total (mg/1)	Bottom Sediment (mg/1)	Maximum in Sediment Deposits (mg/kg)	Plankton (μg/g)	Benthos (μg/g)	Total Steady-State Accumulation (kg)
Pond	1.0kg hr^{-1}	1.5	1.6	1.5	$1.6x10^3$	$4.7x10^3$	$4.7x10^3$	$1.1x10^3$
Eutrophic Lake	1.0kg hr^{-1}	0.14	0.16	0.11	44	$4.3x10^2$	$3.4x10^2$	$1x10^3$
Oligotrophic Lake	1.0kg hr^{-1}	0.15	0.17	$3.2x10^{-2}$	7.1	$4.6x10^2$	97	$5.3x10^2$
River	1.0kg hr^{-1}	$9.7x10^{-4}$	$1x10^{-3}$	$2.2x10^{-4}$	0.15	3	0.68	3.1
Turbid River	1.0kg hr^{-1}	$9x10^{-4}$	$1x10^{-3}$	$4.5x10^{-4}$	$9.2x10^{-2}$	2.8	1.4	2.4
Coastal Plain River	1.0kg hr^{-1}	$9.3x10^{-3}$	$9.6x10^{-3}$	$2.8x10^{-3}$	4.2	29	8.5	66

---

[a] All data simulated by EXAMS model (see text for further information).

TABLE 4-9. THE FATE OF 1,2,4-TRICHLOROBENZENE IN VARIOUS GENERALIZED AQUATIC SYSTEMS[a]

System	% Residing in Water at Steady-State 1	% Residing in Sediment at Steady-State	% Transformed by Chemical Processes	% Transformed by Biological Processes	% Volatilized	% Lost by other Processes[b]	Time for System Self-Purification[c]
Pond	3	97	0	0.05	91.2	8.7	579 days
Eutrophic Lake	38	62	0	2.2	92.8	5	472 days
Oligotrophic Lake	83.2	16.8	0	0	94.2	5.8	195 days
River [d]	30	70	0	0	1.3	98.7	62 days
Turbid River [d]	37.4	62.6	0	0	1.2	98.8	49 days
Coastal Plain River [d]	12.5	87.5	0	0.3	12.1	87.9	87 days

---

[a] All data simulated by the EXAMS model (see text for further information).

[b] Including loss through physical transport out of system.

[c] Estimate for removal of Ca 75% of the toxicant accumulated in system. Estimated from the results of the half-lives for the toxicant in bottom sediment and water columns, with overall cleansing time weighted according to the toxicant's initial distribution.

[d] All river systems are 3 km in length so that physical transport out of the modelled system is dominant loss process. The "river" system was extended to various lengths up to 1000km from the source to determine the significance of other fate processes (see text).

compared with that in the pond and eutrophic lake was responsible for the shorter purification time due to a smaller amount of the chemical being adsorbed. As would be expected, under equilibrium conditions 62-97% of the 1,2,4-trichlorobenzene mass resided in the sediment, while sediment adsorption accounted for less than 17% of the mass in the oligotrophic lake. Chemical oxidation of 1,2,4-trichlorobenzene was negligible in all systems. Only in the biologically active eutrophic system was biodegradation responsible for a noticeable loss, albeit still less than 3% of the total mass.

In the river ecosystems, physical transport out of the model's 3-km long box was more significant than in the other systems. From 62 to 87% of the 1,2,4-trichlorobenzene mass in a river stretch resided in the sediment. Chemical and biological processes were insignificant. Volatilization did not become an important factor in 1,2,4-trichlorobenzene loss until 50 km downstream from the source of release, at which point it accounted for approximately 45% of the trichlorobenzene loss. More than 95% of trichlorobenzene was volatilized at a distance of 500 km downstream.

The average concentration of 1,2,4-trichlorobenzene (total) in water was approximately 1 mg/l in the pond and lakes and approximately 1-10 µg/l in the rivers. Concentrations were higher in the higher biomass coastal plain river. Levels in bottom sediment were generally two to three orders of magnitude above water concentrations, with biomass concentrations usually three orders of magnitude greater still. The significance of biomass as a reservoir for 1,2,4-trichlorobenzene (note biomass/water partition coefficient of 3×10^3 in Table 4-10), is reflected in the higher values for total steady-state accumulation in eutrophic than oligotrophic lake and coastal plain than other river systems. (Biota and sediment may both be significant as described more fully in Section 4.1.3.5.)

Based on the output of the EXAMS simulation and depending on the model assumptions and reliability of input variables, the following conclusions can be drawn about 1,2,4-trichlorobenzene's potential environmental fate in aquatic systems. Persistence is a function of volatilization. The half-lives of 1,2,4-trichlorobenzene (under conditions of continuous discharge) are listed in Table 4-10. The half-lives for the other river systems modeled are not included because only 3-km lengths were simulated, so that physical export was responsible for over 85% of removal. Persistence would be greater in the coastal plain river due to higher biomass. Since volatilization is so important in all systems, then conditions of high temperatures, high wind velocity, turbulence, and low biomass would increase the transfer of trichlorobenzene to the atmosphere in real systems. This assumes negligible transformation of the compound in both liquid and vapor form. The rate of biodegradation may be greater and more competitive with volatilization under realistic environmental conditions - especially conditions conducive to acclimation - than the rate of 1×10^{-10} mole/l/hr used as input.

TABLE 4-10. SYSTEM HALF-LIVES FOR 1,2,4-TRICHLOROBENZENE PERSISTENCE

System	$t_{1/2}$
Oligotrophic Lake	15 days
Eutrophic Lake	29 days
Pond	65 days
River	7 days[a]

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[a] In a 500-km stretch of river.

Source: U.S. EPA (1980c)

4.3.5 Concentrations Detected in Ambient Surface Waters

The STORET Water Quality System is the principal data source for 1,2,4-trichlorobenzene in ambient waters (U.S. EPA 1980a). As is the case with effluent concentrations (Section 4.3.2), all STORET observations for ambient water are remarked data. There were 310 observations of 1,2,4-trichlorobenzene in ambient waters in various sections of the U.S., as shown in Table 4-11. Approximately 86% of the observed concentrations were lower than 10 μg/1. In five major river basins, there were observations between 10 μg/1 and 100 μg/1, accounting for roughly 11% of the total. Most observations within this range occurred in the California basin. In the Missouri River basin, eight observations were reported in the range of 100 μg/1 to 1000 μg/1. From just over 300 observations recorded (remarked) for the compound in the ambient water, the mean is calculated to be 22.7 μg/1, the maximum concentration 1000 μg/1.

Fischer and Slemrova (1978) studied the pollution of surface waters with chlorobenzene by taking a longitudinal concentration profile of the Rhine River in Germany. The concentration of trichlorobenzene was nearly constant in the middle segment of the river, being less than 100 ng/1. In the lower segment of the river, however, the concentration increased to 500 ng/1.

Hites (1973) examined water samples from the Merrimack River in New England downstream of industrial sites and five urban areas. Trichlorobenzene was identified at concentrations of 0.1-0.5 μg/1, along with other compounds commonly used in the textile industry (which was represented in the area).

Grob and Grob (1974) analyzed various water samples in the area of Zurich. Trichlorobenzene registered at 6 ng/1 in surface water and at 42 ng/1 from a depth of 30 m. A concentration of 4 ng/1 was recorded for trichlorobenzene in tap water samples; the compound was not detected in spring and groundwaters.

Selected data on concentrations of 1,2,4-trichlorobenzene observed in ambient waters in the U.S. are summarized in Table 4-12.

4.3.6 Ambient Concentrations Reported in Other Aquatic Systems

Results from STORET (U.S. EPA 1980a) indicate the following:

- Concentrations in estuaries of the Gulf Coast and San Francisco Bay areas are reported as less than 10 μg/1.
- Concentrations were not detected in well waters of Kansas, Washington, Arizona and six southern states; detection limits ranged from 1 to 50 μg/1.

TABLE 4-11. DISTRIBUTION OF REMARKED AMBIENT 1,2,4-TRICHLOROBENZENE CONCENTRATIONS FOR MAJOR RIVER BASINS IN THE UNITED STATES--STORET, 1980

	Number of Observations	% at Concentration (μg/1)			
		≤10	10.1-99.9	100.1-999.9	≥1000
Northeast					
North Atlantic	6	6			
Southeast	75	52	23		
Tennessee River					
Ohio River	54	51	3		
Lake Erie					
Upper Mississippi	12	12			
Lake Michigan					
Missouri River	43	35		8	
Lower Mississippi	9	9			
Colorado River	3		3		
Western Gulf	15	15			
Pacific Northwest	86	86			
California	100		100		
Great Basin	1		1		
Puerto Rico	1	1			
Virgin Islands					
Lake Superior					
Unlabelled	1	1			
UNITED STATES	310	286	130	8	

Source: STORET Water Quality Control Information System, retrieved on October 28, 1980.

Note: Remarked are all values between 0 and the detection limits.

TABLE 4-12. AMBIENT SURFACE WATER CONCENTRATIONS OF 1,2,4-TRICHLOROBENZENE

Source/Location	Concentration (μg/l)	Reference
Los Angeles River Urban Runoff (Winter)	0.007	Young _et_ _al._ (1976)
Merrimack River, downstream of Concord and Manchester, NH, and Lowell, Lawrence and Haverhill, MA: samples taken April 1972 and January 1973	0.1-0.5	Hites (1973)
Delaware River at Philadelphia March 1977. None detected in samples taken in August 1976	0.5-1.0	Sheldon and Hites (1978)

- Analysis of 108 sediment samples taken in the southern and western regions of the U.S. yielded remarked concentrations less than reporting limits.

4.4 ATMOSPHERIC FATE

No information was found regarding the atmospheric releases by users of 1,2,4-trichlorobenzene. Herbicide and pesticide use of the chemical may constitute a significant atmospheric release and may be important in terms of human exposure.

4.4.1 Photodegradation

In the atmosphere 1,2,4-trichlorobenzene is apparently photodegraded fairly rapidly. This rate appears to be rapid enough to prevent accumulation (Simmons et al. 1977). Experimental studies suggest that several mechanisms for the photodegradation of 1,2,4-trichlorobenzene exist, but it is difficult to extrapolate the laboratory reaction rates to rates expected in the environment.

The most rapid photodegradative mechanism for 1,2,4-trichlorobenzene seems to be attack by the hydroxyl radical. Hydroxyl radicals are believed to be formed by a series of photochemical reactions involving No, NO_2, other atmospheric hydrocarbons, and HO_2 (Calvert 1976). Specific investigations of this mechanism with respect to 1,2,4-trichlorobenzene have not been widely reported. Dilling et al. (1976) observed that 43% of the monochlorobenzene disappeared in 7.5 hours from an initial concentration (10 ppm) (molar basis) under simulated atmospheric conditions. If this is extrapolated to 50% disappearance and corrected for ambient light intensity, the estimated half-life for the atmospheric photodecomposition of monochlorobenzene is 23 hours. A variety of substituted benzenes (not including any chlorobenzenes) were determined by Darnall et al. (1976) to belong to a class of compounds that have atmospheric half-lives between 0.24 and 24 hours.

Photodechlorination is a possible mechanism for atmospheric degradation of 1,2,4-trichlorobenzene (Akermark et al. 1976, and Akermark 1978). Irradiation by ultraviolet light in the 300-nm range (as is found in the atmosphere) results in the removal of a chlorine atom from the 1,2,4-trichlorobenzene, which is replaced by a hydrogen atom from the solvent. In the experiments performed by Akermark, 2-propanol was the hydrogen-donating solvent. Although Akermark observed that 20% of the initial quantity of 1,2,4-trichlorobenzene was dechlorinated (to dichlorobenzene) in 70 minutes, it is difficult to extrapolate this rate to a expected rate under atmospheric conditions, particularly because of the low natural abundance of the required hydrogen donors in the atmosphere. Although Akermark states that, "Prolonged irradiation of [1,2,4-trichlorobenzene] will ultimately lead to complete dehalogenation," (Akermark 1978), the rate at which the initially-formed dichlorobenzenes will be dechlorinated further is unknown. Photodechlorination, then, may be an important atmospheric degradative pathway, but its contribution cannot be quantified.

Photoformation of polychlorinated biphenyls from 1,2,4-trichlorobenzene (and from other chlorinated benzenes) was observed by Uyeta et al. (1976). Although this reaction is not likely to account for very much 1,2,4-trichlorobenzene in the atmosphere, it may be of interest due to the nature of the products. Twenty grams of a chlorobenzene in a sealed glass flask were exposed to the sun for 56 days. Under these conditions, 1,2,4-trichlorobenzene produced the greatest quantity of PCBs compared with any of the other nine chlorobenzenes studied. The 1,2,4-trichlorobenzene flask contained 5,710 mg/l of PCBs after 14 days of irradiation, and after 56 days of irradiation, the concentration of PCBs in the flask was nearly 17%. This reaction consists of two interacting chlorobenzene molecules. The conditions of pure undiluted chlorobenzene, which produced the large amounts of PCBs noted above, highly favor PCB production more than the normal atmospheric conditions in which part-per-billion or part-per-trillion levels of 1,2,4-trichlorobenzene occur. For this reason, atmospheric production of PCBs from 1,2,4-trichlorobenzene does not seem likely to account for a significant portion of the fate of 1,2,4-trichlorobenzene in the atmosphere.

4.4.2 Wet and Dry Deposition

Ten measurements of the dry deposition of 1,2,4-trichlorobenzene at five locations in southern California were made during the fall of 1975 and the spring of 1976 (Young et al. 1976). The largest median value reported was <20 ng/m^2 per day from six collections at one location during the fall of 1975. The median value of all ten observations is reported as <11 ng/m^2 per day. Due to the low atmospheric concentrations of 1,2,4-trichlorobenzene, it is not expected that wet or dry deposition is a significant pathway for 1,2,4-trichlorobenzene.

4.4.3 Atmospheric Monitoring

The non-point releases dispersed throughout the United States combined with rapid atmospheric dilution, probably preclude the detection of 1,2,4-trichlorobenzene by ordinary analytic methods. The few reports of observed concentrations indicate extremely low ambient 1,2,4-trichlorobenzene concentrations in the atmosphere. At 16 sites around the U.S., air monitoring data indicate levels of 1,2,4-trichlorobenzene below the detection limits (ranging from 10 ng/m^3 to 100 ng/m^3). The only exceptions were at several monitoring sites specifically chosen in the vicinity of chemical industry facility around which there were known to be atmospheric concentrations of various chemical compounds. At several of these chemical plants and dump sites, 1,2,4-trichlorobenzene was observed, however, these concentrations were all below 167 μg/m^3 and are not assumed to be representative of ambient concentrations (Pellizzari 1978).

4.5 TERRESTRIAL FATE

4.5.1 Introduction

A large portion (some 36%) of the estimated environmental releases of 1,2,4-trichlorobenzene are to land (see Chapter 3.0). The primary source of land release is disposal of used electrical equipment containing 1,2,4-trichlorobenzene bearing fluids. Other sources include use of pesticides and herbicides containing 1,2,4-trichlorobenzene, and disposal of treated sludge from various industries. Consequently, the land is a significant pathway for 1,2,4-trichlorobenzene. The available data on the fate of the compound on land are insufficient for a full evaluation of this pathway, however, within the constraints of the data, the following topics are discussed: adsorption by soil, volatilization, biodegradation and leaching to groundwater.

4.5.2 Adsorption onto Soil

Though some portion of the 1,2,4-trichlorobenzene in soil will be adsorbed onto the soil particles, this phenomenon will compete with volatilization and biodegradation. The Freundlich equation yields a value of 22 mg adsorbed 1,2,4-trichlorobenzene per kilogram of soil [assuming a soil absorption coefficient of 11,000, a soil organic content of 2% and a 1,2,4-trichlorobenzene concentration of 0.1 mg/l in the water above the soil (Fiksel and Segal 1980)]. The material that is adsorbed by soil either persists in the soil or is biodegraded.

Volatilization is a competing force in the moist portion of the soil column. The strength of this force is dependent upon temperature, the extent of aeration, and the presence of microbial organisms. (Volatilization is more fully discussed in Section 4.3.3.1.)

4.5.3 Biodegradation

The two most important biological processes with respect to 1,2,4-trichlorobenzene are biodegradation, which "removes" the compound through transformation to other substances; and bioaccumulation, which stores the compound temporarily and may or may not be concurrent with metabolism of the substance. Bioaccumulation is discussed in Section 4.3.3.2 and biodegradation is discussed below.

There is laboratory evidence that trichlorobenzene is degraded under aerobic conditions. Table 4-13 presents the results of several biodegradation studies on the compound. In general, the studies produce similar results and indicate a rapid, initial spurt of biodegradation within the first few days. Some metabolic intermediates apparently build-up and the break-down of these, as well as the degradation of the remainder of the initial trichlorobenzene, occurs at a rate slower than the initial rate. None of the studies were allowed to proceed long enough to determine the period of time needed for ultimate degradation of 1,2,4-trichlorobenzene to CO_2, H_2O, and minerals.

TABLE 4-13. MICROBIAL BIODEGRADATION OF 1,2,4-TRICHLOROBENZENE

<table>
<tr><th>Microbial Population Source and Type</th><th>Type of Study</th><th>Results</th><th>Source</th></tr>
<tr><td>Sandy loam soil, unacclimated, aerobic</td><td>Closed flask</td><td>Degradation rate 1.0 n mol./day (per 20 gm. soil)</td><td>Marinucci and Bartha (1979)</td></tr>
<tr><td>Soil in liquid culture, unacclimated</td><td>Shake flask</td><td>Degradation rate 7.1± 0.6 n mol./day</td><td>Marinucci and Bartha (1979)</td></tr>
<tr><td>Sewage sludge in liquid culture, unacclimated and acclimated</td><td>Static flask</td><td>Tested at 5 and 10 mg/l, first in unacclimated culture, then in 3 successive subcultures each seeded with the preceeding culture. Table below presents percent degraded in 7 days.
<table>
<tr><th></th><th></th><th colspan="3">Subcultures</th></tr>
<tr><th>Conc. (mg/l)</th><th>Unacclimated</th><th>1</th><th>2</th><th>3</th></tr>
<tr><td>5</td><td>54%</td><td>70%</td><td>59%</td><td>24%</td></tr>
<tr><td>10</td><td>43%</td><td>54%</td><td>14%</td><td>0</td></tr>
</table></td><td>Tabak et al. (1980)</td></tr>
<tr><td>Wastewater population unacclimated</td><td>BOD bottles</td><td>55% degraded in 10 days (based on TOD decline).</td><td>Simmons et al. (1977)</td></tr>
<tr><td>Wastewater population unacclimated</td><td>$14CO_2$ evolution in aerated closed flasks</td><td>1) 33% of trichlorobenzene was converted to CO_2 in one day, 56% in 5 days. Maximum degradation rate was 40 mg/gMLVS/day.
2) Mass balance of trichlorobenzene at 120 hrs. was 56% converted to CO_2, 7% volatilized, 23% to polar metabolites, 13% remaining as trichlorobenzene.</td><td>Simmons et al. (1977)</td></tr>
</table>

Little attempt has been made to identify the degradation products of 1,2,4-trichlorobenzene. Figure 4-2 presents a proposed partial degradation pathway determined by C^{14}-labeling (Marinucci and Bartha 1979). Identifiable intermediate products included 2,4-, 3,5-, and 3,4-dichlorophenol and 3,5-dichlorocathechol.

Since trichlorobenzene is volatile, soil with high organic content would tend to reduce losses through volatilization and retain the compound longer; the opportunity for biodegradation would be longer in such soils. Additional organic matter in Marinucci and Bartha's (1979) soil experiment had no impact on the rate of biodegradation itself.

4.5.4 Soil to Groundwater: A Field Study

The U.S. EPA (1976) described an accidental spill of 1,500 gal of transformer fluid, which contained a mixture of chlorinated organics including 1,2,4-trichlorobenzene and other chlorobenzenes. Soil and groundwater monitoring data in the areas around the spill revealed that the trichlorobenzene component of the solvent migrated quickly out of the spill area, through the soil, and into the local groundwater supplies. The higher chlorinated benzenes were observed to be retained preferentially in the soil around the spill areas and migrated much more slowly than the trichlorobenzenes. A 236-ft well adjacent to the spill areas showed "solvent" concentrations of 1 μg/l in the groundwater 2 years after the spill, compared with an initial groundwater concentration of 500 μg/l.

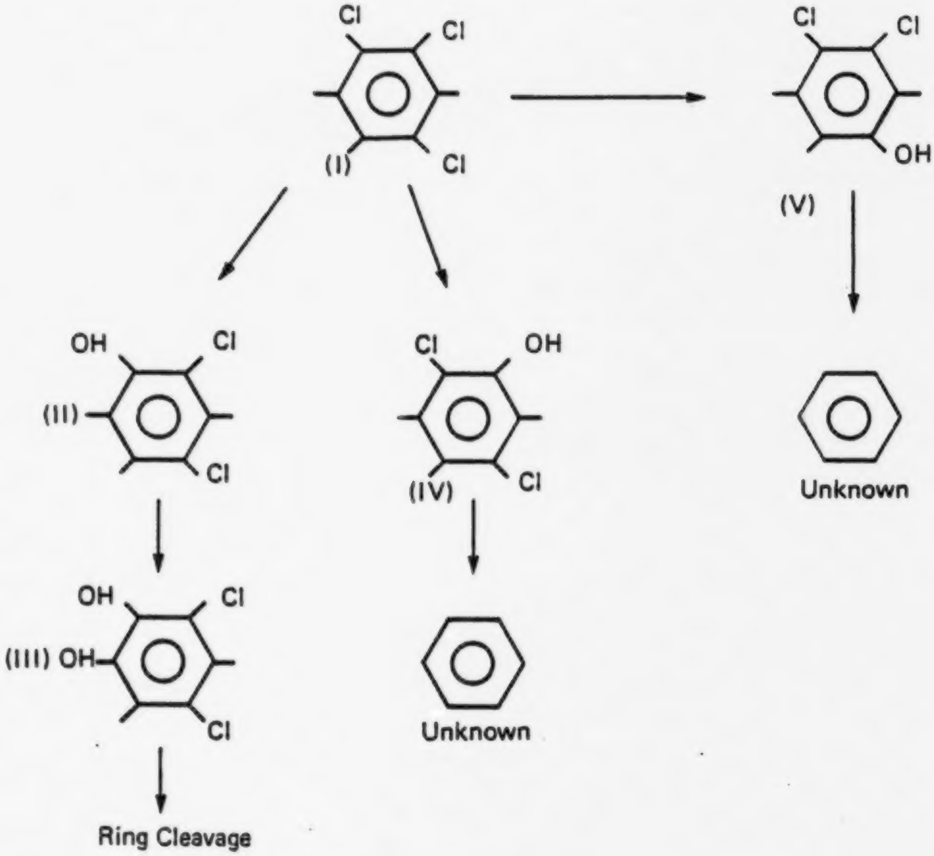
The presence of detectable concentrations of solvent observed 2 years after the spill might suggest that soil degradation is very slow, but it must be noted that an unusually large amount of solvent was spilled.

4.6 FATE IN POTWs AND OTHER WATER TREATMENT FACILITIES

4.6.1 Wastewaters

Removal efficiencies ranging from 13% to 100% have been reported for 1,2,4-trichlorobenzene in POTWs and water treatment plants. Specific observations of 1,2,4-trichlorobenzene concentrations in influent and effluent are listed in Table 4-14.

Simmons et al. (1977) performed laboratory biodegradation experiments using radiolabeled 1,2,4-trichlorobenzene and activated sludge from an industrial secondary wastewater plant. The results (see Table 4-13) indicated rapid biodegradation in the first day and 50% degradation by 5 days; the experiment did not continue long enough to determine the fate of the remaining intermediate metabolic products which were not degraded to CO_2 during the study period. The study suggests that biological treatment can be an effective removal process for


Cl
Cl
(I)
Cl
Cl
Cl
OH
(V)
OH
Cl
(II)
Cl
Cl
OH
Cl
(IV)
Unknown
OH
Cl
(III) OH
Cl
Unknown
Ring Cleavage

I	1,2,4-trichlorobenzene
II	2,4-dichlorophenol
III	3,5-dichlorocatechol
IV	2,5-dichlorophenol
V	3,4-dichlorophenol

Source: Marinucci and Bartha (1979).

FIGURE 4-2 PROPOSED BIODEGRADATION PATHWAY FOR 1,2,4-TRICHLOROBENZENE

TABLE 4-14. TRICHLOROBENZENE REMOVAL EFFICIENCIES OF SELECTED WASTEWATER TREATMENT FACILITIES[a]

Sample Source	Concentration (μg/1) Influent	Concentration (μg/1) Effluent	References
Sewage treatment plant/ Ohio River.	66.9	57.9	Bellar et al. (1974)
Wastewater treatment plants handling industrial effluents in Philadelphia, Pennsylvania	60 1 9 43	0 1 1 13	Gaffney (1976)
Northeast Sewage Treatment Plant handling industrial effluents in Philadelphia, Pennsylvania.	20	10	Sheldon and Hites (1979)

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[a] Unspecified isomer.

1,2,4-trichlorobenzene in wastewater treatment. Another result of the study was that after 5 days, only 7% of the original quantity of 1,2,4-trichlorobenzene had volatilized. Throughout the experiment, about 80% of the 1,2,4-trichlorobenzene present was associated with sludge solids, which slowed down the rate of volatilization.

Wroniewicz (1978) described a wastewater treatment study in which biological treatment was among several alternatives investigated. Biological treatment was determined "unsuitable" as a wastewater treatment alternative due to the necessity for very long retention times and the accumulation of organics in the sludge. Treatment with activated carbon was found to be the best method for organics removal.

Brandon and Samfield (1978) reported on an advanced wastewater treatment method which, although not commercially available at this time, has been shown to be very effective for the removal of many types of pollutants, including organic compounds with molecular weights ≥ 90. Trichlorobenzene (unspecificed isomer) at 100 mg/l (100 ppm) is reported to be rejected at greater than 99% by a "PA-200 poly (ether/amide) thin-film composite membrane" at 1,000 psi and at 25°C. Brandon and Samfield also report that the use of such filtration may be economically viable at full scale.

During the summer and winter seasons of 1976, Heesen and Young (1977) collected daily grab samples of final effluent from the five largest dischargers of municipal wastewater to the Southern California Bight. Effluent samples were analyzed using solvent extraction methods and electron-capture gas chromatography techniques. The average concentrations of 1,2,4-trichlorobenzene ranged from 0.18 μg/l to 100 μg/l in the summer season and from 0.25 μg/l to 43 μg/l in the winter season for five regions of Southern California.

Gaffney (1976) gathered information on various processing chemicals and their concentrations in municipal wastewaters and water supplies. The study was conducted in northwest Georgia, where a great number of tufted textile industry plants operate in a single river basin. Water and wastewater samples were collected during the fall and winter of 1974. At three water treatment facilities, concentrations of trichlorobenzene (non-isomer specific) ranged from 0.1 mg/l to 1.1 mg/l in raw waters and from 0.1 mg/l to 1 mg/l in finished waters; concentrations in winter samples were 0.1 mg/l and 0.1 to 1.1 mg/l in fall samples. These concentrations were significantly above the detection limit of 0.2 μg/l and appeared to increase in a downstream pattern. In wastewater samples, trichlorobenzene concentrations ranged from 1 μg/l to 1,297 μg/l in influent samples and from 0 to 13 μg/l in final effluent samples.

In conclusion, biological treatment facilities seem to be the most efficient at removing 1,2,4-trichlorobenzene from waste streams. Treatment efficiencies of other systems vary from 30% to 100%.

4.6.2 Effects of Chlorination During Water Treatment

Under certain laboratory conditions, 1,2,4-trichlorobenzene is formed during the chlorination of wastewater. In water treatment systems, no observations were found of 1,2,4-trichlorobenzene formation from the chlorination of drinking water.

Gaffney (1977) studied the effects of chlorination on wastewater containing biphenyl. The concentration of 1,2,4-trichlorobenzene in wastewater influent, when chlorinated in the presence of biphenyl, increased from 0.9 μg/l to 2.9 μg/l. Effluent from an industrial wastewater treatment plant subjected to the same conditions also showed an increase from 0.3 μg/l to 1.0 μg/l. Gaffney noted that the concentrations of biphenyl and chlorine used in his experiments "were comparable to those which may be encountered in normal operation of wastewater treatment facilities in the area under investigation."

Glaze and Henderson (1975) obtained effluent samples before chlorination from a Texas sewage treatment plant. These samples were filtered and then chlorinated by bubbling chlorine gas through stirring aliquots for 1 hour. After this intense chlorination treatment, trichlorobenzene was identified qualitatively by mass spectrometry, but the concentration was below the level necessary for quantification.

Bellar et al. (1974) studied the formation of organohalides during the chlorination process at a treatment facility near the Ohio River. Trichlorobenzenes were among the seven organochlorine compounds in water from a sewage treatment facility that serves a large industrial area and a municipality. A concentration of 66.9 μg/l was recorded for trichlorobenzenes in influent before treatment. Trichlorobenzenes in effluent samples registered at 56.7 μg/l before chlorination and increased slightly to 56.9 μg/l after chlorination.

Thus it appears that small amounts of 1,2,4-trichlorobenzene may be formed during chlorination of certain wastewaters. It is likely that the formation of 1,2,4-trichlorobenzene is dependent upon the presence of specific precursors, such as biphenyl. If this is true, the formation of 1,2,4-trichlorobenzene may be less likely to occur during the chlorination of drinking water where the water is fairly clean and free of organics.

4.6.3 Concentrations Detected in Drinking Water

The National Organics Monitoring Survey (NOMS) conducted sampling of drinking water systems in 113 communities throughout the United States (U.S. EPA undated). The survey was conducted in three phases over a 12-month period and sampled water supplies for various organics, including 1,2,4-trichlorobenzene; these supplies represented different types of sources and treatment processes. The detections of 1,2,4-trichlorobenzene found in the survey are presented in Table 4-15. The compound was only detected in 11 of the 113 cities surveyed. The most

TABLE 4-15. OCCURRENCE OF 1,2,4-TRICHLOROBENZENE IN COMMUNITY DRINKING WATER SUPPLIES

Community	Concentration (μg/l)		
	Phase I March-April 1976 (112 Supplies Sampled)	Phase II May-July 1976 (113 Supplies Sampled)	Phase III November 1976-January 1977 (110 Supplies Sampled)
Cape Girardeau, MO	10.0	-	0.03
Chicago, IL	-	-	0.01
Erie, PA	-	-	0.01
Huntington, WV	-	-	0.03
Jacksonville, FL	-	0.006	n.d.5
Louisville, KY	-	0.58	0.53
Passaic Valley, NJ	-	-	0.03
Richmond, VA	-	-	0.23
Santa Fe, NM	-	-	0.01
Boston, MA	-	-	0.01
Toledo, OH	-	-	0.01
Mean, Standard Deviation	-	-	0.09 ± 0.1687

Note: Where values were not presented, 1,2,4-trichlorobenzene was not detected; n.d.5 indicates that 1,2,4-trichlorobenzene was not found with detection limits of 5 μg/l.

Source: U.S. EPA (undated).

frequent occurrence was in Phase III (November 1976 through January 1977), in which 1,2,4-trichlorobenzene was found in waters from 10 communities at concentrations ranging from 0.01 μg/l to 0.53 μg/l with a mean of 0.09 μg/l. In Cape Girardeau, MO, 1,2,4-trichlorobenzene was also detected once during Phase I (March-April, 1976) at an elevated concentration of 10.0 μg/l. It was also detected in Jacksonville, FL and Louisville, KY during Phase II (May-July 1976) at 0.006 μg/l and 0.58 μg/l, respectively.

Sheldon and Hites (1978) identified roughly 100 organic compounds in Delaware River water samples collected in August 1976 and March 1977 between Marcus Hook, PA and Trenton, NJ. This segment of the river was selected because it is a direct source of drinking water for several cities in the region and is the most heavily industrialized area along the river. The concentration range for trichlorobenzene was 0.5 μg/l to 1 μg/l in the winter; trichlorobenzenes were not detected during the summer.

The transport of industrial organic chemicals from their source in the Delaware River, via various treatment facilities and into Philadelphia's drinking water supply was investigated by Sheldon and Hites (1979). The segment of the Delaware River examined flows through a heavily industrialized area and is dominated by tidal movement as opposed to downstream river flow. These conditions allow industrial chemicals to be transported from sewer outfall upstream to the intake pipe of a drinking water facility. Several compounds appeared to originate at a number of plants in the area; the concentration of trichlorobenzenes at one plant site registered at 200 μg/l though the plant may not be the sole contributor of trichlorobenzenes in the river system. At a sewage treatment plant downstream, trichlorobenzenes registered at 20 μg/l in influent samples and at 10 μg/l in final effluent samples. At two sampling points before the drinking water facility, only trace amounts of trichlorobenzenes were detected. In both influent and effluent samples at the drinking water treatment facility, as well as downstream from the facility, none of the trichlorobenzene isomers were detected.

Coleman et al. (1980) used the closed-loop-stripping technique to examine the effect of a granular activated carbon filter on the removal of organic compounds in drinking water. The granular activated-carbon filter was implemented at a treatment facility. The 1,2,4-trichlorobenzene isomer was recorded at 8 ng/l in influent samples. After the initial use of the filter (allowing 1 million gallons of water to pass through the filter) 1,2,4-trichlorobenzene was not detected in the effluent. After a month had elapsed with the same filter in place, 1,2,4-trichlorobenzene was not detected in the effluent samples; it had been registered at 5 ng/l in influent samples.

4.7 SUMMARY

The compound 1,2,4-trichlorobenzene is released to all of the environmental media, with land and the aquatic environment the largest receptors. The resulting pathways are illustrated in Figure 4-3.

The inherent stability of 1,2,4-trichlorobenzene allows it to persist for a long time in the soil before its ultimate degradation. With the exception of biomagnification, this persistence has associated with it the effect of greatly diluting the chemical before it is degraded. This dilution, along with the relatively small usage of 1,2,4-trichlorobenzene, precludes good observations of these ultimate degradation mechanisms. An exception to this may be biodegradation, however, the potential of this is reduced by biomagnification.

Nearly 52% of the initial 1,2,4-trichlorobenzene releases are to surface waters and POTWs, primarily by the textile-dyeing industry. A portion of the amount released to surface water is rapidly volatilized to the atmosphere. The magnitude of this rapid volatilization is unknown and probably varies greatly depending upon the presence of adsorbing matter and degree of aeration. A large portion of the 1,2,4-trichlorobenzene will rapidly volatilize from distilled water, within a matter of hours under aerated conditions and within a few days under static conditions. No information was available on natural waters; however, in surface water with a considerable amount of suspended organic sediment and biomass, volatilization will be very slow and biological pathways and biodegradation will become important.

Monitoring data available in the STORET Water Quality System report all observations of 1,2,4-trichlorobenzene in ambient waters as remarked data, that is, observed at levels below the detection limits. The compound was observed infrequently in ambient waters throughout the U.S. and then only in low concentrations. Higher concentrations were found in the vicinity of industrial effluents and POTW discharges.

In biological treatment facilities with high concentrations of suspended biota, volatilization of 1,2,4-trichlorobenzene at an initial concentration of 345 μg/l has been shown to be very insignificant (7% after 5 days). Under conditions simulating a biological treatment plant, biodegradation has effectively degraded most of the 1,2,4-trichlorobenzene. After 5 days, 65% was converted to CO_2 and 32% was converted to polar metabolites. In practice, however, total removal efficiencies vary from 13% removal to 100% removal (variation is likely to occur due to adsorption by biota).

Freshwater sediments are capable of adsorbing 1,2,4-trichlorobenzene depending upon the amount of organic matter in the sediment and the concentration of the chemical in the water. Based on the Freundlich equation, a river containing 0.1 mg of 1,2,4-trichlorobenzene per liter

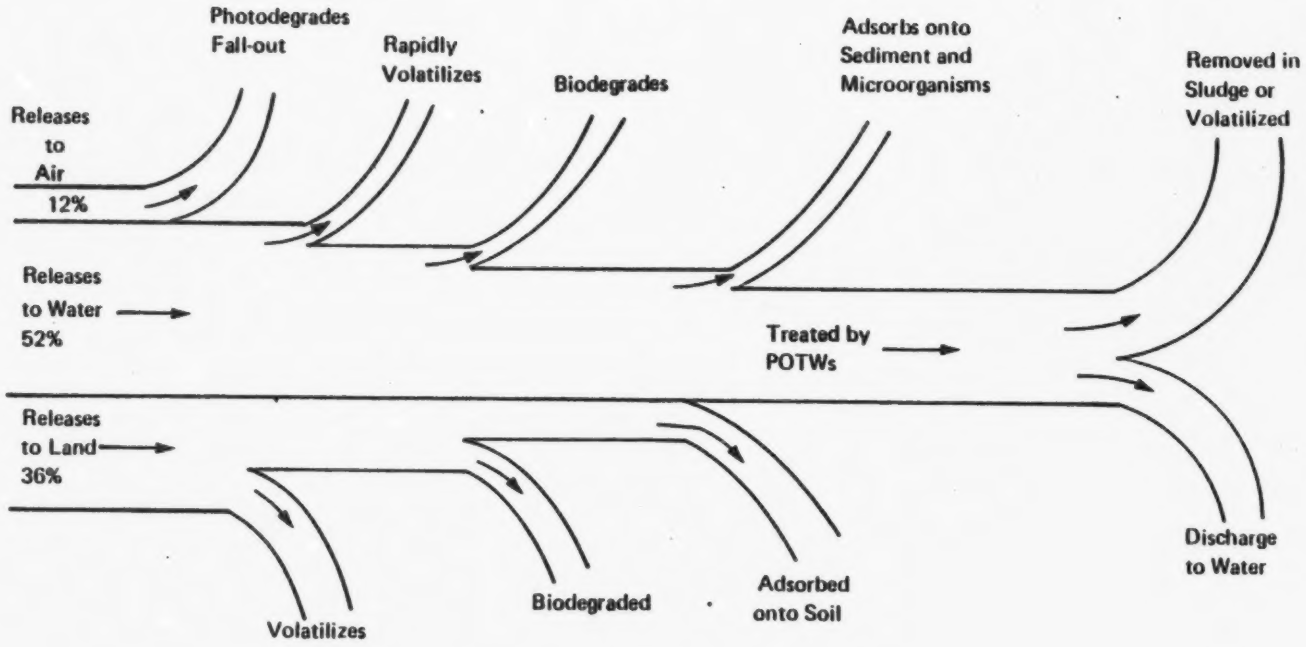
Releases
to
Air
12%
Photodegrades
Fall-out
Rapidly
Volatilizes
Biodegrades
Adsorbs onto
Sediment and
Microorganisms
Removed in
Sludge or
Volatilized
Releases
to Water
52%
Treated by
POTWs
Releases
to Land
36%
Discharge
to Water
Volatilizes
Biodegraded
Adsorbed
onto Soil

FIGURE 4-3 ENVIRONMENTAL PATHWAYS OF 1,2,4 - TRICHLOROBENZENE

(kilogram) of water would have an associated surface sediment concentration of approximately 20 mg 1,2,4-trichlorobenzene per kg of sediment. This medium is essentially a sink for some quantity of 1,2,4-trichlorobenzene, although biodegradation does occur slowly.

Biodegradation of 1,2,4-trichlorobenzene does occur in laboratory soil incubation studies, but it is not known if the rate of biodegradation under field conditions is fast enough to prevent the chemical from making its way into groundwater at sites of release.

Inasmuch as 1,2,4-trichlorobenzene has never been observed in sustained high concentrations in the atmosphere (even in the industrial areas), it is likely that the amount of the chemical that is released to the atmosphere, either from direct emissions or as a result of volatilization from surface water, photodegrades at a rate which is at least equal to the rate of release. The primary mechanism for photodegradation appears to involve photolytically generated hydroxyl radicals. Other mechanisms such as photochlorination and biphenyl formation also exist, 1,2,4-trichlorobenzene is rarely observed in the atmosphere. Air samples at two chemical plants producing 1,2,4-trichlorobenzene revealed concentrations around 100 ng/m^3 infrequently.

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5.0 EXPOSURE AND EFFECTS -- HUMANS

5.1 HUMAN TOXICITY

5.1.1 Introduction

Data on the carcinogenicity, teratogenicity, mutagenicity, and long-term oral toxicity of 1,2,4-trichlorobenzene are generally lacking. Thus, no reliable estimates can be made concerning the effects of long-term exposure to low levels of this compound in drinking water. The available data on the effects of 1,2,4-trichlorobenzene are discussed in the following sections.

5.1.2 Metabolism and Bioaccumulation

The 1,2,4-isomer of trichlorobenzene is slowly absorbed from the gastrointestinal tract, skin, and lungs. In mammals, the primary metabolic pathway for 1,2,4-trichlorobenzene is via oxidation to phenols (2,3,5- and 2,4,5-trichlorophenols) and subsequent conversion to the glucuronide and sulfate conjugates; little or no catechol or mercapturic acid formation occurs with the trichlorinated benzenes (Williams 1959).

In rabbits, oral administration of 500 mg/kg of 1,2,4-trichlorobenzene resulted in the urinary excretion of 42% of the dose as phenols (2,3,5- and 2,4,5-trichlorophenols), 38% as glucuronic and ethereal sulfate conjugates, 0.3% as 2,3,4- or 2,3,5-trichlorophenyl mercapturic acids, and a trace amount of 3,4,6-trichlorocatechol (Williams 1959). Jondorff and coworkers (1955) similarly reported that 38% of a 500-mg/kg oral dose of 1,2,4-trichlorobenzene was metabolized to phenols by rabbits and excreted in urine within 5 days of dosing. By the intraperitoneal route, approximately 11% of a single 60-75-mg/kg dose of 1,2,4-trichlorobenzene administered to male rabbits was excreted as phenols (5% as 2,4,5- and 6% as 2,3,5-trichlorophenol) in the urine by 10 days (Kohli *et al*. 1976). A half-life of 5.5 days has been estimated for 1,2,4-trichlorobenzene in the rabbit (Parke and Williams 1960).

In the rat, Smith and Tardiff (1978) noted that over 85% of either an oral or intravenous dose -- 10 mg/kg bw (body weight) -- of ^{14}C labelled 1,2,4-trichlorobenzene was excreted in the urine, with the remainder recovered in feces. The tissue content of trichlorobenzene and metabolites reportedly varied little with route of administration; the highest tissue concentrations were found in kidney, fat, liver, and plasma (values not given). The data also suggested that 1,2,4-trichlorobenzene undergoes extensive enterohepatic circulation in the rat.

Smith and Carlson (1979) reported that fecal excretion of 1,2,4-trichlorobenzene in the rat was only 5-10% of urinary excretion following oral administration of 1 mmole (180 mg)/kg/day for 7 days; urinary excretion values were not given.

In the rhesus monkey, only 30-40% of a 10-mg/kg intravenous dose of radiolabelled 1,2,4-trichlorobenzene was excreted (time period unspecified); elimination was principally via the urine (27-36% of the dose), with lesser amounts in the feces. The same dose given orally was reported to result in considerably more radioactivity in the urine. No values were given. Blood concentrations of trichlorobenzene were also reported to be generally lower and more persistent in monkeys than in rats. Again, no values were given (Smith and Tardiff 1978).

Kohli and associates (1976) have proposed that 1,2,4-trichlorobenzene is metabolized by means of an arene oxide intermediate via the NADPH-cytochrome P-450 microsomal enzyme system; this pathway, however, has not been demonstrated experimentally. Egyankor and Franklin (1977) have reported that the 1,2,4-isomer enhances the hepatic mixed-function oxidase system. The compound has also been demonstrated to be an inducer of xenobiotic metabolism in rats (Carlson et al. 1979, Carlson 1978, Carlson and Tardiff 1976, Smith and Carlson 1979, Ariyoshi et al. 1975a, b).

5.1.3 Human and Animal Studies

5.1.3.1 Carcinogenicity

No adequate studies have been conducted on the possible carcinogenic effects associated with 1,2,4-trichlorobenzene exposure. Goto et al. (1972) reported no increased incidence of hepatomas above controls in 20 male ICR-JCL strain mice fed 1,2,4-trichlorobenzene at a level of 600 mg/kg diet for 6 months. (Note: USEPA Criteria Document incorrectly states that exposure was by inhalation.) The mice were killed at 6 months. If one assumes that the stated dosage is given as a weight/weight ratio, then a daily intake of 72 mg 1,2,4-trichlorobenzene/kg bw/day can be estimated for a 25-g mouse ingesting on average 3 g diet/kg/bw/day.

This shorter-than-lifetime study is inadequate for the assessment of carcinogenic risk.

5.1.3.2 Mutagenicity

Two mutagenicity studies utilizing the bacterium *Salmonella typhimurium* reported negative results, with or without metabolic activation by liver microsomes, in strains TA 100, TA 1535 (base-pair mutants) and TA 98, TA 1537, TA 1538 (frameshift mutants) for 1,2,4-trichlorobenzene at concentrations up to 140 mg/plate (Andersen et al. 1972, Schoeny 1978, 1979).

Schoeny (1977) also points out that pretreatment of animals with 1,2,4-trichlorobenzene can influence the mutagenesis of other compounds by its ability to induce mixed-function oxidases.

5.1.3.3 Adverse Reproductive Effects

Studies on the possible teratogenic or reproductive effects caused by 1,2,4-trichlorobenzene exposure could not be found.

5.1.3.4 Other Toxic Effects

Chronic ingestion studies conducted with 1,2,4-trichlorobenzene could not be found. Cragg et al. (1978) and Smith et al. (1978) noted no evidence of toxicity with respect to body weight changes, hematology, clinical chemistry, cytochrome P-450 or P-448 induction, or gross pathology in rhesus monkeys given oral doses of 1-25 mg/kg 1,2,4-trichlorobenzene for 120 days. Doses of 90 mg/kg or above were toxic, while doses of 174 mg/kg were lethal within 20-30 days. At doses of 125 mg/kg, temporary weight loss and evidence of hepatic enzyme induction was indicated by a shift in the urinary pattern of chlorguanide metabolites and increased clearance of intravenous doses of labelled 1,2,4-trichlorobenzene. Animals receiving the highest dosage (174 mg/kg) exhibited severe weight loss and fine tremors, which were most pronounced a few days before death. Terminally, they had elevated levels of urea N, Na, K, CPK, SGOT, SGPT, LDH, and alkaline phosphatase, as well as hypercalcemia and hyperphosphatemia; there was no evidence of jaundice. Nonlethal clinical signs and biochemical changes were quickly reversed when treatment was discontinued.

Subchronic exposure to 1,2,4-trichlorobenzene by inhalation was studied in Sprague-Dawley rats, New Zealand white rabbits, or cynomolgus monkeys (Macaca fascicularis) by Coate et al. (1977). These authors reported no exposure-related effects on body weight, hematology or serum biochemical determinations including BUN, total bilirubin, SGOT, SGPT, alkaline phosphatase, and LDH after 4, 13, or 26 weeks of inhalation exposure to 200,400, or 800 mg/m^3 1,2,4-trichlorobenzene, 7 hours per day, 5 days per week. In addition, no exposure-related ophthalmic changes or detectable microscopic changes in the liver and kidneys were observed in either rabbits or monkeys. Monkeys tested after 26 weeks of exposure exhibited no dose-related changes in static compliance, CO diffusion capacity, distribution of ventilation, or lung volumes. Three indicators of operant behavior indicated no dose-related changes in monkeys at all tested doses after 26 weeks of exposure. Transient liver and kidney effects were noted in rats after both 4 and 13 weeks, but had disappeared by 26 weeks of exposure. These transient changes included dose-dependent enlargement of individual hepatocytes, and dose-independent increases in the degree of vacuolation of hepatocytes, slight increases in the degree of biliary hyperplasia, hyaline degeneration in the inner zone of the cortex of the kidney, and slight increases in incidence and degree of granuloma formation in the livers (the latter had disappeared by 13 weeks). Although these effects were transient in nature, the fact that slight changes in parenchymal hepatic and renal cells of rats were evident after only 4 weeks of intermittent exposure to 200 mg/m^3 1,2,4-trichlorobenzene suggests a need for additional studies.

Watanabe et al. (1978) reported indications of induction of hepatic porphyria in rats following a study of inhalation by rats, dogs and rabbits of 80, 240 or 800 mg/m^3 1,2,4-trichlorobenzene, 7 hrs/day, 5 days/week for 30 exposures. At concentrations of 240 mg/m^3 and 800 mg/m^3, elevated urinary excretion and uroporphyrin and coproporphyrin were noted in rats, and both dogs and rats exhibited increased liver weights at the 800-mg/m^3 level. Inhalations of 800 mg/m^3 1,2,4-trichlorobenzene, 6 hrs/day, 5 days/week for 3 months, produced slightly increased urinary uroprophyrin excretion over 90 days in rats. This increase, however, disappeared 2-4 months after exposure ceased. The no adverse effect level in rats was 24 mg/m^3. No significant effects on body weight, hematology, or gross or microscopic pathology were demonstrated in any of the three animal species at any dose level.

In similar studies, Rimington and Ziegler (1963) were able to induce experimental hepatic porphyria in three male rats given 730 mg/kg bw of 1,2,4-trichlorobenzene by gavage (maximum tolerated dose) daily for 15 days. Urinary coproporphyrin excretion was increased (58.3 µg/day vs. 4.3-6.8 µg/day in controls). Urinary porphobilinogen (PBG) excretion was also elevated (197 µg/day) above the control values (2.5-6.5 µg/day). The porphyria could be reversed by glutathione administration. Hair loss due to follicular hyperkeratosis was also noted.

Carlson (1977) reported increased liver weights, but no induction of hepatic porphyria in rats following oral administration of 50, 100 or 200 mg/kg 1,2,4-trichlorobenzene daily for 30, 60, 90 or 120 days. Increases in liver porphyrins minimally increased after 200 mg/kg for 30 or 90 days, but urinary excretion of ALA and PBG was not elevated at any dose regardless of duration of exposure.

The compound 1,2,4-trichlorobenzene could not be considered hepatotoxic, as judged by serum isocitrate dehydrogenase activity, following oral administration of 150, 300 or 600 mg/kg/day to rats for 14 days. Liver glucose-6-phosphatase activity decreased with doses of 300 mg/kg/day or greater, but were not affected at 150 mg/kg/day. Doses of 600 mg/kg/day 1,2,4-trichlorobenzene were not lethal even after 14 days of administration (Carlson and Tardiff 1976).

For acute exposures, Rowe (1975) reported minor eye and respiratory irritation in humans when exposed to 24 mg/m^3 or 40 mg/m^3 1,2,4-trichlorobenzene vapor but not to 19.2 mg/m^3.

Acute oral LD_{50} values of 756 (556-939) mg/kg and 766 (601-979) mg/kg 1,2,4-trichlorobenzene have been reported for rats and mice, respectively, with deaths delayed 3-5 days after dose administration. Animals exhibited depressed activity at sublethal doses and extensor convulsions prior to death at lethal concentrations. (Brown et al. 1969). The lowest lethal dose reported for intraperitoneal injection of 1,2,4-trichlorobenzene in mice is 500 mg/kg (RTECS 1978).

Yamamoto et al. (1978) reported dermal LD_{50} values for 1,2,4-trichlorobenzene in ddY strain mice of 300 mg/kg and 305 mg/kg (male and female, respectively). An acute toxic percutaneous dose of 6,139 mg/kg 1,2,4-trichlorobenzene was reported for rats by Brown et al. (1969). Irritation to the skin was minor, although fissuring typical of a defatting action was observed after prolonged contact in rabbits and guinea pigs. Spongiosis, acanthosis, and parakeratosis were noted in both species, along with some inflammation of the superficial dermis in rabbits exposed daily for 3 weeks. Some guinea pigs exposed to 0.5 ml/day 1,2,4-trichlorobenzene, 5 days/week for 3 weeks exhibited necrotic lesions of the liver and death after extensor convulsions (Brown _et al_. 1969).

Yang _et al_. (1979) reported a more than 900% increase in bile-duct pancreatic-fluid (BDPF) flow and a more than 50% reduction in its protein concentration 24 hours after intraperitoneal injection of 5 mmoles (900 mg)/kg 1,2,4-trichlorobenzene into male Holtzman rats. BDPF chloride concentration and serumic glutamic pyruvic transaminase (SGPT) activity were not significantly changed, but hepatic bile flow was increased. The mechanism by which 1,2,4-trichlorobenzene increases BDPF flow is not known, but it is not produced by secretin or cholinergic stimulation of the pancreas; nor was liver damage essential for the increased flow to occur.

5.1.4 Summary of Human Effects Considerations

5.1.4.1 Ambient Water Quality Criterion -- Human Health

The position of the U.S. Environmental Protection Agency (1980) is that there are insufficient toxicological data on the health effects of 1,2,4-trichlorobenzene to establish a toxicological criterion for preventing adverse effects in man.

5.1.4.2 Health Effects Considerations

The general lack of data on the carcinogenicity, teratogenicity, mutagenicity and long-term oral toxicity of 1,2,4-trichlorobenzene (see Table 5-1) does not allow one to estimate reliably the effects of long-term human exposure to low levels of 1,2,4-trichlorobenzene. No data on human exposure effects are available other than reports of eye and respiratory irritation occurring at concentrations of 24 mg/m^3, but not at 19 mg/m^3.

Animal data indicate that 1,2,4-trichlorobenzene is slowly absorbed from the gut, skin and lung and metabolized to phenols, probably via an arene oxide intermediate. The phenols, in conjugated form, are excreted, principally via the urine.

Subchronic studies with rhesus monkeys suggested little effect on the liver, hematological parameters, or clinical chemistries at levels of 25 mg/kg/day orally for 120 days. Signs of toxicity became evident at 90 mg/kg, with lethality occurring within 20-30 days in animals given 174 mg/kg/day.

Similar results were reported for rats, rabbits, and dogs exposed by inhalation to concentrations up to 800 mg 1,2,4-trichlorobenzene/m^3, 7 hrs/day, 5 days/week for 30 exposures. Experimental hepatic porphyria (which is

TABLE 5-1. ADVERSE EFFECTS OF 1,2,4-TRICHLOROBENZENE ON MAMMALS AND BACTERIA

Adverse Effect	Species	Lowest Reported Effect Level	No Apparent Effect Level
Carcinogenicity	- - -	No data available	- - -
Teratogenicity/ Reproductive Effects	- - -	No data available	- - -
Mutagenicity	*Salmonella*		140 mg/plate
Disturbances in hematology, clinical chemistries, liver pathology	rhesus monkey	90 mg/kg/day orally	25 mg/kg/day orally for 120 days
	dog	- -	800 mg/m^3,7 hr/day, 5 d/wk for 30 exposures
	rat	- -	
Hepatic porphyria (reversible)	rat	240 mg/m^3, 7 hr/day 5 d/wk for 30 exposures	24 mg/m^3, 7 hr/day, 5 d/wk for 30 exposures
Median oral lethal dose	rat	LD_{50} = 756 mg/kg	- - -

Source: Data taken from Section 5.1 of this report.

Note: These data are taken from studies that were not presented in sufficient detail to allow extrapolation of human dose response relationships for 1,2,4-trichlorobenzene. These data should not be considered as threshold human effects levels.

reversible when exposure ceases) has been induced in rats given 730 mg/kg/day 1,2,4-trichlorobenzene by gavage for 15 days, but not in rats given 200 mg/kg daily for 120 days. No other data are available.

None of this information is sufficient to estimate dose-response relationships for humans to 1,2,4-trichlorobenzene with any degree of reliability.

5.2 EXPOSURE

5.2.1 Introduction

As a man-made compound produced in relatively low volumes, 1,2,4-trichlorobenzene has been found infrequently and in low concentrations throughout the human environment. The most common route of human exposure is by ingestion of drinking water and food. Concentrations of 1,2,4-trichlorobenzene are infrequently detected in the air and then only at low concentrations. As a result, exposure through inhalation is not expected to be significant. There is no evidence to indicate that percutaneous exposure occurs or is significant.

5.2.2 Exposure Routes

5.2.2.1 Exposure through Ingestion

Man may ingest 1,2,4-trichlorobenzene in drinking water or in food. The chemical occurs in water as a result of its use in industrial processes. The textile industry is the largest consumer and identified discharger of 1,2,4-trichlorobenzene in the United States to water (both surface water and POTWs). The U.S. EPA has identified releases of 1,2,4-trichlorobenzene from steam electric power plants, foundries, and the non-ferrous metals industry. Concentrations of 1,2,4-trichlorobenzene detected in the effluents associated with these industries range from 4.4 μg/l to 2700 μg/l as reported in Table 4-14. Because of the occurrence of 1,2,4-trichlorobenzene in industrial discharges to POTWs and because some treatment processes are not efficient at removal of 1,2,4-trichlorobenzene, the chemical is found in POTW effluents. Specific sites of discharge from POTWs, industries and surface runoff with effluents containing 1,2,4-trichlorobenzene were monitored in different seasons of the year as shown in Table 4-3. Surface runoff into the Los Angeles River contained 0.007 μg/l 1,2,4-trichlorobenzene in the winter; data for the other seasons were not given. Municipal wastewaters were monitored across the country in the summer and in the fall: typically the concentrations were from 2 to 20 times higher in the summer (0.23 to 275 μg/l) than in the fall (< 0.01 to 130 μg/l). Levels of 1,2,4-trichlorobenzene in industrial discharges in North Carolina in the summer and Tennessee in the spring averaged 12 μg/l and 500 μg/l, respectively.

The presence of 1,2,4-trichlorobenzene in surface waters, as identified above, suggests the possible 1,2,4-trichlorobenzene contamination of drinking water systems and marketable fish species, which are the principal potential contributors to human exposure through ingestion.

In the Water Quality Criterion Document (U.S. EPA 1980), the highest reported concentration of 1,2,4-trichlorobenzene in drinking water was 1.0 μg/l.

The National Organics Monitoring study (U.S. EPA und.) was conducted in three phases throughout a one-year period. The results with respect to 1,2,4-trichlorobenzene are presented in Table 4-15. In the first phase, 1,2,4-trichlorobenzene was detected once out of 112 samples at a concentration of 10 μg/l. Typical concentrations in the other samples were in the range of 0.006 μg/l to 0.58 μg/l. The 10 positive samples (greater than the detection limits) of Phase III were observed with a median of 0.02 μg/l. The daily intake of 1,2,4-trichlorobenzene resulting from consumption of drinking water contaminated with the highest levels would be 1.16 to 20 μg/day, assuming an average adult water consumption of 2.0 liters per day (ICRP 1975). Using the median value (0.02 μg/l) the average adult would consume 0.04 μg/day.

Fish that were taken from 1,2,4-trichlorobenzene contaminated waters and consumed are a potential source of ingested 1,2,4-trichlorobenzene. U.S. EPA (1980) reported that trout taken from Lake Superior and turbot taken from Lake Huron contained measurable concentrations of trichlorobenzene (unspecified isomer). There were no data available that identified concentrations of 1,2,4-trichlorobenzene in edible species of fish, and consequently, the ingestion of 1,2,4-trichlorobenzene associated with human consumption of fish cannot be evaluated.

5.2.2.2 Exposure through Inhalation

Atmospheric releases of 1,2,4-trichlorobenzene are a small portion of total environmental releases (see Chapter 3.0). Futhermore, following atmospheric release, it is likely that 1,2,4-trichlorobenzene is rapidly diluted and/or photodegraded (see Chapter 4.0). Air monitoring at 16 sites throughout the United States indicated that 1,2,4-trichlorobenzene typically occurred below the detection limits of 10 to 100 ng/m^3. At isolated chemical plants and in the vicinity of waste dumping sites, 1,2,4-trichlorobenzene was occasionally detected at levels of 167 ng/m^3 or lower (Pellizzari _et al_. 1978), however those levels are not representative of the environment. During a study of aerial dry deposition in southern California in which 5 samples were taken, median levels of 1,2,4-trichlorobenzene were consistently less than 11 $ng/m^2/day$ (U.S. EPA 1980)..

For the small populations in the immediate vicinity of chemical plants or dumpsites potentially exposed to concentrations of 1,2,4-trichlorobenzene, average intake by inhalation would be a maximum of 240 ng/hour during a worst-case exposure. This assumes an average adult breathing rate of 1.4 m^3/hour (ICRP 1975). Exposure to 1,2,4-trichlorobenzene via inhalation for the general population is expected to be much lower to the point of being insignificant.

5.2.2.3 Percutaneous Exposure

The only identified source of 1,2,4-trichlorobenzene to which the human skin is potentially exposed in the non-occupational environment is as a result of dry deposition from the atmosphere (noted above). In that absorption of liquid 1,2,4-trichlorobenzene is slow, no dermal absorption via atmospheric deposition is not expected to be a significant route.

5.2.3 Summary

Exposure to 1,2,4-trichlorobenzene does not appear to be significant due to the low concentrations found throughout the environment. Except in areas with industrial activity in which 1,2,4-trichlorobenzene is found in aquatic discharges and atmospheric releases, 1,2,4-trichlorobenzene is generally not detected. There were sufficient data available to estimate worst-case air and drinking water exposures and these are presented in Table 5-2. It should be noted that these estimates are based on limited data and are not representative of widespread exposure in the United States.

TABLE 5-2. ESTIMATED EXPOSURE TO ELEVATED LEVELS OF 1,2,4-TRICHLOROBENZENE[a]

Exposure Route	Median Concentration	Maximum Concentration	Mean Intake	Maximum Intake
Drinking Water	0.2 µg/l[b]	10.0 µg/l	0.4 µg/day[c]	20.0 µg/day[c]
Inhalation	below 10 ng/m^3	167 ng/m^3	below 14 ng/hour	240 ng/hour[d]

a. Estimates based upon the infrequent, elevated 1,2,4-trichlorobenzene concentrations, which were the only observations reported.

b. Median was calculated on the basis of concentrations above detection limits and is not representative of all U.S. drinking water systems.

c. Drinking water intake assumes an average daily drinking water consumption of 2.0 liters per day for adults.

d. Inhalation intake is based on an average adult respiratory rate of 1.4 m^3/hour while awake (ICRP 1975).

Note: These estimates are based upon limited data and not believed to represent widespread exposure in the U.S. Information on levels of 1,2,4-trichlorobenzene in foods was unavailable, and consequently exposure through ingestion of foods was not evaluated.

Source: Arthur D. Little, Inc. 1981.

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6.0 EFFECTS AND EXPOSURE--AQUATIC BIOTA

6.1 EFFECTS ON AQUATIC BIOTA

The laboratory data concerning the acute toxicity of 1,2,4-trichlorobenzene for aquatic species are very limited; the data concerning chronic effects are even more limited. For all of the other chlorinated benzenes, there are considerable data that can be used to extrapolate general trends in toxicity and bioaccumulation. Overall, toxicity and bioconcentration in aquatic organisms increase with increasing chlorination of the compound (from monochlorobenzene), with pentachlorobenzene being the most toxic (U.S. EPA 1980a).

Data concerning acute and chronic toxicity of 1,2,4-trichlorobenzene are presented in Tables 6-1 and 6-2. These data are from recent compilations (U.S. EPA 1978; U.S. EPA 1980b), and are believed to reflect the extent of what is available at present.

The most sensitive species from these data are the mysid shrimp (LC_{50} of 0.45 mg/l) and rainbow trout (1.5 mg/l); the most resistent is Daphnia, with an LC_{50} of 50.2 mg/l. Chronic effects levels range from 200 μg/l to 700 μg/l. A bioconcentration factor of 182 has been reported for bluegill (U.S. EPA 1978).

6.2 EXPOSURE

STORET monitoring data (Section 4.3) indicate that the majority of observed concentrations in both ambient and effluent samples from major U.S. river basins were less than 10 μg/l (80% < 10 μg/l ambient; 72% < 10 μg/l effluent). The mean ambient concentration is 22.7 μg/l; the mean concentration in the effluents is 12 μg/l. Approximately 10 ambient observations were greater than 100 μg/l. The balance of the effluent concentrations were from 10-100 μg/l.

Concentrations of 1,2,4-trichlorobenzene in effluents from municipal wastewaters, industrial dischargers and urban runoff were reported in various parts of the U.S. In one study these ranged from 0.01 μg/l to 275 μg/l in the summer and fall, with one discharge as high as 500 μg/l in the spring in Tennessee (see Table 4-3). Effluents from the textile industry, steam electric power plants, foundries, and non-ferrous metal industry were sampled with 1,2,4-trichlorobenzene concentrations ranging from means of 1 μg/l to 410 μg/l and maxima of 260 μg/l to 2700 μg/l in raw waste effluents (see Table 4-5). Treated waste effluents sampled in the same analysis ranged from 4.4 μg/l to 610 ug/l on the average to maximums of 47 μg/l to 1500 μg/l, also shown in Table 4-5. Data simulated by EXAMS model (see Section 4.3.4) assume an environmental loading of 1,2,4-trichlorobenzene of 1.0 kg/hr into various generalized aquatic systems. As shown in Table 4-8, maximum concentrations in water simulated were 1 μg/l in the river, 160 μg/l in eutrophic lakes, 170 μg/l in oligotrophic lakes, and 1600 μg/l in ponds.

TABLE 6-1. ACUTE TOXICITY OF 1,2,4-TRICHLOROBENZENE FOR FRESHWATER AND SALTWATER SPECIES

Species	Test Method[a]	LC_{50} (mg/l)	EC_{50} (mg/l)	Reference
Freshwater:				
Cladoceran (*Daphnia magna*)	S,U	50.2		U.S. EPA (1978)
Rainbow trout (*Salmo gairdneri*)	FT,M	1.5		U.S. EPA (1980b)
Fathead minnow (*Pimephales promelas*)	FT,M	2.87		U.S. EPA (1980b)
Bluegill sunfish (*Lepomis macrochirus*)	S,U	3.36		U.S. EPA (1978)
Alga (*Selenastrum capricornutum*)			35.3 (chlorophylla) 26.7 (cell numbers)	U.S. EPA (1978)
Saltwater:				
Mysid shrimp (*Mysidopsis bahia*)	S,U	0.450		U.S. EPA (1978)
Sheepshead minnow (*Cyrpinodon variegatus*)	S,U	21.4		U.S. EPA (1978)
Alga (*Skeletonema constatus*)			8.7(96-hr, chlorphylla) 8.9(96-hr, cell numbers)	U.S. EPA (1978)

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[a] S,U = static, unmeasured; FT,M = flow through, with measured concentrations.

TABLE 6-2. CHRONIC TOXICITY OF 1,2,4-TRICHLOROBENZENE FOR FRESHWATER SPECIES

	Test Method[a]	Habitat[b]	Limits (μg/l)	Chronic Value (μg/l)	Reference
Fathead minnow *Pimephales promelas*	embryo-larval	FW	200-410	286	U.S. EPA (1978)
Fathead minnow	ELS	FW	499-995	705	U.S. EPA (1980b)
Sheepshead minnow *Cyprinodon variegatus*	ELS	SW	150-330	222	U.S. EPA (1978)

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[a] ELS = Early life stage.

[b] FW = Fresh water
SW = Salt water

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7.0 RISK CONSIDERATIONS

This chapter evaluates the human and non-human risk associated with exposure to 1,2,4-trichlorobenzene based upon available effects data and known exposure levels in the environment that were documented in Chapter 5.0 and 6.0.

7.1 HUMAN RISK

The risk of adverse human effects due to exposure to ambient levels of 1,2,4-trichlorobenzene through ingestion, inhalation, or percutaneous exposure cannot be reliably evaluated at this time due to insufficient data in two areas. First, there is a general lack of data on the carcinogenicity, teratogenicity, mutagenicity, and long-term oral toxicity of 1,2,4-trichlorobenzene. Available human data are limited to reported eye and respiratory irritation following acute exposure to 1,2,4-trichlorobenzene. Second, since there is a general lack of data concerning levels of the compound in air, surface water, soil, and groundwater, it is not possible to quantify with any degree of certainty the levels to which humans are exposed.

7.1.1 Human Health Considerations

On the basis of the available animal data on health effects of 1,2,4-trichlorobenzene, there is little evidence of adverse health effects resulting from exposure to the low levels of 1,2,4-trichlorobenzene believed to occur in the environment. None of the animal studies, however, provided sufficient data for extrapolating estimates of dose-response relationships to humans.

Animal data indicate that 1,2,4-trichlorobenzene is slowly absorbed from the gut, skin and lung, and metabolized to phenols, probably via an arene oxide intermediate. The phenols, in conjugated form, are excreted, principally via the urine.

Subchronic studies with rhesus monkeys suggested little effect on the liver, hematological parameters, or clinical chemistries at levels of 25 mg/kg/day orally for 120 days. Signs of toxicity become evident at 90 mg/kg, with lethality occuring within 20-30 days in animals given 174 mg/kg/day (Cragg et al. 1978, Smith et al. 1978).

Similar results were reported for rats, rabbits, and dogs exposed by inhalation to concentrations up to 800 mg trichlorobenzene/m^3, 7 hrs/day, 5 days/week for 30 exposures (Watanabe et al. 1978). Experimental hepatic porphyria (which is reversible when exposure ceases) has been induced in rats given 730 mg/kg/day 1,2,4-trichlorobenzene by gavage for 15 days (Rimington and Ziegler 1963), but not in rats given 200 mg/kg daily for 120 days (Carlson 1977).

There were reports of human eye and respiratory irritation occurring at atmospheric concentrations of 1,2,4-trichlorobenzene of 24 mg/m^3, but not at 19 mg/m^3 (Rowe 1975). There were no other human or animal data available.

7.1.2 Routes of Exposure

7.1.2.1 Inhalation

Inhalation of ambient air is not expected to expose humans to significant quantities of 1,2,4-trichlorobenzene. When released to the atmosphere as a result of industrial activity, the concentration of 1,2,4-trichlorobenzene is rapidly decreased by photodegradation of dry deposition (fallout). Consequently it does not persist in ambient air long enough to be detected or to be inhaled by humans for any length of time. One study sampled the air at the point of emissions release from two chemical plants, detecting 1,2,4-trichlorobenzene concentrations around 100 ng/m^3 (Pellizzari 1978). However, following rapid dilution, the resulting concentration would be far less in the human environment in a community with such a 1,2,4-trichlorobenzene emitting facility.

Levels of 1,2,4-trichlorobenzene in the ambient atmosphere are far below the no-apparent-effect-level in rats of 24 mg/m^3 for 7 hours a day for a 5-day week reported in Watanabe et al. (1978). Therefore inhaled 1,2,4-trichlorobenzene is not likely to constitute a human health risk due to the low levels found in the ambient atmospheric environment.

The reported human eye irritations occurred following exposure to 24 mg/m^3 but not to 19 mg/m^3. These levels are orders of magnitude above the worst case atmospheric exposure at the point of emission from a chemical plant. Consequently, risk of human eye irritation due to exposure to 1,2,4-trichlorobenzene at ambient air levels can be considered to be negligible.

7.1.2.2 Ingestion

There are no reliable dose-response data for ingestion of 1,2,4-trichlorobenzene in drinking water and food. The only identified significant route of ingested 1,2,4-trichlorobenzene is from drinking water . The compound has been identified in several U.S. community water supplies at a median concentration of 0.02 μg/l (U.S. EPA undated). One study identified 1,2,4-trichlorobenzene at the site of a spill and found that it persisted in nearby groundwater; however, no other data could be found to indicate what concentrations occur in groundwaters tapped for drinking supplies or at what frequency. Finally, 1,2,4-trichlorobenzene has been detected in high concentrations in selected industrial effluent waters (see Section 4.3). If drinking water intakes were located nearby or downstream of effluents, associated drinking waters might be contaminated with 1,2,4-trichlorobenzene; there are no data to evaluate this potential exposure.

Because of the lack of information on human health effects levels and limited exposure data, the human health risk associated with ingestion of 1,2,4-trichlorobenzene cannot be evaluated at this time.

7.1.3 Conclusions

The risk associated with exposure to 1,2,4-trichlorobenzene is uncertain for ingestion of contaminated drinking water. The exposure associated with inhalation of 1,2,4-trichlorobenzene is expected to be minimal due to the extremely low levels occurring in ambient air; however, risk associated with inhalation can not be reliably determined on the basis of existing animal data.

7.2 NON-HUMAN RISK

The available data on concentrations of 1,2,4-trichlorobenzene in environmental media and on effects levels for aquatic biota are extremely limited. Although some chronic and acutely toxic effects of 1,2,4-trichlorobenzene have been observed, the concentrations eliciting these responses are generally well above those reported for ambient waters. A water quality criterion has not been established by the U.S. EPA to protect freshwater aquatic life because of the insufficiency of data (U.S. EPA 1980a); it must be noted, however, that most data that is available is from studies performed outside the United States and is based in part on effects data for other chlorinated benzenes. The limited monitoring data suggest that a level of 30 μg/l (suggested criterion in the Soviet Union) is rarely exceeded in ambient waters, but may be exceeded in the vicinity of industrial effluent discharges.

7.2.1 Exposure

In order to determine the potential risk to aquatic organisms due to 1,2,4-trichlorobenzene exposure, it is necessary to compare effects levels to ambient levels. The STORET Water Quality System and data available in the literature indicate that the majority of ambient concentrations detected in waters were below 10 μg/l for ambient waters (U.S. EPA 1980b). There were roughly 10 ambient observations between 100 and 1000 μg/l, i.e., above the threshold for chronic effects, all of which occurred in the Missouri basin.

Higher concentrations of 1,2,4-trichlorobenzene were reported in the vicinity of industrial effluents. Maximum observations were in the range of 47 μg/l to 270 μg/l, the latter of which is in the range of producing adverse effects to organisms (see Section 4.3). There are no data that indicate that the compound persists for a significant period of time in surface waters. In fact much of the compound presumably volatilizes quite rapidly. No fish kills have been reported in any areas throughout the U.S. (U.S. EPA, personal communication 1980).

7.2.2 Aquatic Effects and Risk Considerations

The threshold levels for toxic effects for different species range from 1 to 50 mg/l, with only one value below that at 0.45 mg/l. Chronic effects were observed at levels in the range of 200-700 µg/l (U.S. EPA 1980). Much of the data on adverse effects to aquatic organisms are extrapolated from the effects experienced by various species to other chlorinated benzenes. Therefore, it is difficult to evaluate the risk posed to specific species by exposure to 1,2,4-trichlorobenzene. However, if the limited monitoring data are assumed to be representative of widespread environmental conditions, there appears to be little overlap between levels in surface water and effects levels for chlorinated benzenes.

Trichlorobenzene seems to bioaccumulate to a greater extent than some other chlorinated hydrocarbons, but the bioconcentration factor of 182 is not high enough to be considered significant. Since the compound is depurated fairly quickly (<1 day half-life), residues do not appear to be a problem. Overall, aquatic systems are not considered at risk due to exposure to 1,2,4-trichlorobenzene.

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APPENDIX A. ASSUMPTIONS REGARDING ENVIRONMENTAL RELEASES

NOTE 1: There were two U.S. producers of 1,2,4-trichlorobenzene in 1979: Standard Chlorine of Delaware, Inc. in Deleware City and Dow Chemical Company in Midland, Michigan (Davis, 1980; Dickson, 1980). A Standard Chlorine plant official stated that their plant produced 2,880 kkg of 1,2,4-trichlorobenzene (Davis, 1980). In a report submitted to the EPA (and based on the assumption that one-half of the 1,2,3-trichlorobenzene/1,2,4-trichlorobenzene mixed isomer batch was 1,2,4-trichlorobenzene), a total of 8,187 metric tons of 1,2,4-trichlorobenzene were imported and produced; 45 kkg were withdrawn from inventory (Hull and Co., 1980). According to calculations presented in Note 5 in Appendix A, 886 kkg of 1,2,4-trichlorobenzene were imported in 1979. Taking all of these numbers into account, Dow probably produced 8,187 - (2,880 + 886) or 4,221 kkg and the two producers together manufactured 8,187-886 or 7,301 metric tons of 1,2,4-trichlorobenzene for the year 1979.

The U.S. 1,2,4-trichlorobenzene production statistics for 1968-1973 are as follows:

Year	Quantity (kkg)	
	Production	Sales
1968	4,928	5,020
1969	6,901	6,045
1970	4,238	4,322
1971	5,004	5,501
1972	7,039	7,105
1973	12,820	11,881

Source: EPA, 1977a

NOTE 2: Based on process description, approximately 1% of the total quantity of tar produced via the batch process for chlorobenzene manufacture (the same process for which 1,2,4-trichlorobenzene is made) is 1,2,4-trichlorobenzene; see Section 3.2.1.1 for further details.

NOTE 3: Based on the assumption that all of the 1,2,4-trichlorobenzene used as dye carriers is initially sent to water where it may or may not be removed by in-plant treatment procedures; see Section 3.3.1.1 Table 3-2 and Tables B-1 and B-2 (Appendix B) for further details.

NOTE 4: According to Lapp and Sadler (1976), one-half of the release from electrical apparatus impregnation is to air (fugitive emissions) and one-half is discharged to water (handling).

NOTE 5: In 1978, import values of 6,739,685 lbs for all trichloro-, dichloro-, and monochlorobenzene were reported (Harris, 1980). Assuming one-third of this value represents the quantity of trichlorobenzenes imported domestically in 1979, then 2,245,561 lbs or 1,019 kkg were brought into this country for that year.

In 1974, a total of 1,693 kkg of trichlorobenzenes were imported of which 10 kkg (<1%), 427 kkg (25%), and 1,256 kkg (74%) were 1,3,5-, mixed isomers-, and 1,2,4-trichlorobenzene, respectively (EPA, 1977a). If one-half of the trichlorobenzene mixed isomers was 1,2,4-trichlorobenzene, then the total amount of 1,2,4-trichlorobenzene domestically imported in 1974 was about 1,470 kkg, which is 87% of the total trichlorobenzene import value. Therefore, if 87% of the total amount of trichlorobenzene imported into the U.S. in 1979 was 1,2,4-trichlorobenzene, then: 1,019 kkg (0.87) or 886 kkg of 1,2,4-trichlorobenzene were imported in 1979.

NOTE 6: Based on data presented by Lewis (1975), approximately 7% (531 kkg) of the total quantity of 1,2,4-trichlorobenzene used in 1973 was consumed by miscellaneous users. For purposes of this report, miscellaneous uses inlcude all uses other than dye carriers, pesticide intermediates and functional fluids; i.e., miscellaneous uses include: degreasing agents, septic tank and drain cleaners, wood preservatives and abrasive formulations (Hull and Co., 1970; EPA, 1977a). Based on 1979 use patterns for 1,2,4-trichlorobenzene, approximately 80% (424 kkg), 5% (27 kkg), 5% (27 kkg), 10% (53 kkg), and <1% (5 kkg) of the total quantity consumed by miscellaneous users (530 kkg) was used in degreasing agents (i.e., 382 kkg by electronic wafer stripper and 42 kkg for engine cleaners), septic tank cleaners, drain cleaners, wood preservatives and abrasive formulations, respectively (Hull and Co., 1980). Environmental releases from their uses are as follows:

	Quantity Used (kkg)	Environmental Releases[a]			
		Water		Land	Air
		POTW	Surface		
Degreasing Agents					
electronics [b]	382	29		67	190
engines	42				42
Cleaners					
septic tank	27			27	
drain	27	27			
Wood Preservatives [c]	53	1			
Abrasives	<5				

a) Numbers may not add due to rounding; a blank space means <1 kkg released.

b) Electronic wafer cleaning operations used 382 kkg of 1,2,4-trichlorobenzene, of which, an estimated 191 kkg were contained in contaminated waste solvents, of which, 10 kkg were destroyed by incineration, 86 kkg reclaimed, 67 kkg disposed to land, and 29 kkg discharged to POTWs (EPA, 1979c).

c) Fifty-two of the 53 kkg of 1,2,4-trichlorobenzene used in wood preservatives were retained in the wood (Richards, 1980).

NOTE 7: 1,2,4-Trichlorobenzene is also formed by other methods: reacting-benzene hexachloride with calcium hydroxide at 100°C and dehydrohalogenation of α-benzene hexachloride by pyridine (Hardie, 1964). According to an EPA report (1977a), hexachlorobenzene, when reacted with alcoholic caustic potash, will produce 1,2,4-trichlorobenzene. However, because hexachlorobenzene has not been commercially produced for sale since 1976, direct production of 1,2,4-trichlorobenene rom hexachlorobenzene most likely is an obsolete process (SRI, 1980).

NOTE 8: When chlorobenzene is chlorinated, three dichlorobenzene isomers result in the following percentages:

$$\text{Monochlorobenzene} \xrightarrow[\text{catalyst}]{Cl_2} \text{ortho (30\%) + para (70\%) + meta(trace)}$$

NOTE 9: 1,2,4-Trichlorobenzene is manufactured by a batch process as shown in Figure B-1 (Lowenheim and Moran, 1975). Dry benzene is charged into a glass- or lead-lined stirred tank reactor. Either iron turnings or anhydrous ferric chloride are used as a catalyst and remain in the chlorinator after each batch. Chlorine is added to the reactor at such a rate to keep the temperature between 40° and 60°C. If the monochlorobenzene is the desired product, the reaction temperature is maintained at approximately 40°C and about 60% of the stoichiometeric requirement of chlorine used. If poly-substituted chlorobenzenes are desired in addition to monochlorobenzene, the reaction is run at a temperature of 55 to 60°C for approximately six hours.

Hydrogen chloride is recovered by scrubbing with chlorobenzene to remove organic contaminants and absorbing the product gas in a suitable absorption system to give hydrochloric acid. The chlorobenzene product is washed in a stirred reactor with an aqueous solution of sodium hydroxide (10% by weight). A sludge, rich in dichlorobenzenes, settles and is withdrawn for subsequent distillation. After separation of the aqueous layer, the crude reaction product is distilled.

The first two fractions are recycled for further processing. The third fraction contains chlorobenzene which is collected and sent to storage. The fourth fraction, containing primarily dichloro- and 1,2,4-trichlorobenzene, is collected and fractionally distilled to separate the o- and p-dichlorobenzene isomers from 1,2,4-trichlorobenzene (EPA, 1977a; Lowenheim and Moran, 1975).

NOTE 10: A particularly important class of inadvertent sources is found within the chemical industry. Chemical species do not react via single reaction pathway; depending on the nature of the reactive intermediate there are a variety of pathways which lead to a series of reaction products. Often one pathway may be greatly favored over all others, so that by appropriate process design and control of reaction conditions, manufacturers can maximize product yield while minimizing waste production. Therefore, manufacture of a chemical product consists of three steps: (1) combination of reactants under suitable conditions, to yield the desired product; (2) separation of the product from the reaction matrix (e.g., by-products, coproducts and reaction solvents); and (3) final purification of the product. The wastes produced from these separations thus constitute additional sources of chemicals to the environment.

NOTE 11: Even if hexachlorobenzene was manufactured in 1979, 1,2,4-trichlorobenzene most likely would not be released from this source for reasons discussed below. Hexachlorobenzene is usually produced by one of three methods: (1) manufacture of perchloroethylene (contained within by-product tar), (2) reacting benzene (or chlorobenzene) with chlorine (Figures B2 and B3) or (3) treatment of hexachlorocyclohexane isomers with sufuryl chloride. Because the by-product tar from method (1) is known to contain 80% hexachlorobenzene and 10% hexachlorobutadiene, and the remaining 10% is recycled to the process, it is doubtful any 1,2,4-trichlorobenzene would be released to the environment (EPA, 1975b). Method (2) most likely does not release 1,2,4-trichlorobenzene because partially chlorinated benzenes in this process are recycled back to the primary reactors. Furthermore, method (3) could not act as an inadvertent source for 1,2,4-trichlorobenzene because lower chlorinated benzenes are not produced in the process (EPA, 1975b).

NOTE 12: Tetrachlorobenzenes were readily detectable in soil samples collected from a site where tetrachlorobenzene-containing transformer fluid had been spilled seven months earlier. Although a fraction of the tetrachlorobenzenes had been lost (presumably by evaporation and runoff, particularly from the top inch of the affected soil), 43% of the original tetrachlorobenzenes was present in the next lower inch (EPA, 1980b).

NOTE 13: In 1977, approximately 500-4,500 kkg of penthachlorobenzene were produced and converted to pentachloronitrobenzene, a soil fungicide and seed disinfectant. Also, 400 kkg of pentachlorobenzene were produced inadvertently as by-product during the manufacture of other chlorinated benzenes and disposed as waste (Dow, 1979).

NOTE 14: Hexachlorobenzene does not undergo photochemical reactions in the atmosphere and is neither hydrolyzed in aqueous solutions nor broken down by physical, chemical or biological degradation processes occuring in the environment (EPA, 1979a).

NOTE 15: The degradation of lindane to 1,2,4-trichlorobenzene and other compounds by insects, rabbits, and wheat plants has been recognized by Menzie (1969), Karapally and his associates (1973) and

Balba and Saha (1974), respectively. Furthermore, lindane is broken down in soil, presumably by a variety of microorganisms (Mathur and Saha, 1975; Tu, 1976).

NOTE 16: In most textile mills, the 1,2,4-trichlorobenzene dye carrier is only used when specific (usually darker) hues are required. The amount of trichlorobenzene contained in a dye carrier formulation ranges from 10-90% of the total formulation and from <1 - 10% by weight, once added to the dye bath.

NOTE 17: During 1977 and 1978 the EPA collected wastewaters from 50 U.S. textile mills where 1,2,4-trichlorobenzene was found only in those samples originating from wool scouring, woven fabric finishing (simple and complex processing with desizing) and knit fabric finishing operations (EPA, 1979b). This report also discussed 1,165 U.S. wet processing textile mills where 520 performed the aforementioned operations as follows:

			Percent of total
	17	wool scouring	3
	221	woven fabric finishing*	43
	282	knit fabric finshing	54
Total	520		100

In 1979 an estimated 3,490 kkg of 1,2,4-trichlorobenzene were used by domestic textile mills where it is assumed that all of this 1,2,4-trichlorobenzene was discharged to water. If an EPA survey (1979b) is representative of the entire textile industry (which was estimated to consist of 2,000 wet processing mills), and each operation contributes an equal quantity of 1,2,4-trichlorobenzene to wastewaters, then 3, 43, and 54 percent of the total 3,490 kkg used (or 105, 1,501, and 1,885 kkg of 1,2,4-trichlorobenzene) were discharged to water by wool scouring, woven fabric finishing, and knit fabric finishing operations, respectively.

NOTE 18: Dicamba = 3,6-dichloro-2-methoxybenzoic acid; stirofos= 2-chloro-1-(2,4,5-trichlorophenyl)-ethenyl dimethyl phosphate; and trichlorodinitrobenzene = 1,2,4-trichloro-3,5-dinitrobenzene (Sittig, 1977).

NOTE 19: 1,2,4-Trichlorobenzene is used in the production of dicamba as follows: 1,2,4-trichlorobenzene (250 grams, 1.4 mols) and sodium hydroxide (250 grams, 6.3 mols) were dissolved in 1,100 cc of methanol and the solution was charged into a rocking bomb of 4 liter capacity. The solution heated in the sealed bomb at 190°C for 4 hours, during which time the pressure in the bomb rose to 600 psi. The reaction mixturte was removed from the cooled bomb, and the residual solid sodium salt of the phenol was dissolved in hot water, and the solution filtered. The combined aqueous and methanolic solutions were then acidified with hydrochloric acid whereupon an oil separated which was taken up in ether. Drying of the ether solution over magnesium sulphate, filtration, and removal of the ether _in vacuo_ produced an oily residue which on distillation under 2mm pressure gave 2 grams (90% of theory) of an oil boiling at 70°C. The oil solidified on standing to solid 2,5-dichlorophenol (B.pt. 57°C), a compound further processed to make dicamba (Richter, 1961; Sittig, 1977).

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*Assuming two thirds of the total number of woven fabric finishing mills surveyed performed simple and complex processing with desizing.

Stirofos is made by the reaction of trimethyl phosphate with pentachloroacetophenone -- the compound that 1,2,4-trichlorobenzene is incorporated into (Sittig, 1977). To 88 parts of aluminum chloride was added 109 parts of 1,2,4-trichlorobenzene. To this slurry, 88 parts of dichloroacetyl chloride was added over a period of ten minutes with stirring. The mixture then was heated slowly to 90°C where it was held for 4 hours. Decomposition of the complex resulted when the reaction mixture was poured onto a mixture of ice and hydrochloric acid. The resulting mixture was extracted with ether and the organic phase thus obtained was washed successively with dilute hydrochloric acid, water, dilute sodium bicarbonate solution and finally with saturated salt (NaCl) solution. The solvent was evaporated and the residue was distilled to give 134 parts (77% yield) of 2,2,2',4',5'-pentachloroacetophenone (B.pt. 103-105°C; Phillips and Word, 1963; Sittig, 1977).

Trichlorodinitrobenzene is made from 1,2,4-trichlorobenzene and other compounds as follows: a reactor equipped with an agitator, water-cooled condenser, thermometer, liquid feed device, and an external heating and cooling device was charged with 385 parts of a nitrating agent consisting of 18% nitric acid, 73% sulfuric acid and 9% sulfur trioxide. This nitrating agent was warmed to 35°C with stirring and 90.7 parts of 1,2,4-trichlorobenzene added over a period of 30 minutes. The reaction temperature was maintained at 110°C for 6.5 hours at which time the water content of the spent acid was 3%. The reaction mixture was poured into a large volume of water, precipitating 1,2,4-trichloro-3,5-dinitrobenzene in 90.5% yield (Dittmar, 1956; Sittig, 1977).

NOTE 20: As of 1/1/79, dicamba was only made by Northwest Industries, Inc., a subsidiary of Velsicol Chemical Corporation; and Shell Chemical Company was the only producer of stirofos (as of

Note 21: The addition of 1,2,4-trichlorobenzene to dielectric fluids not only increases the viscosity and pour point of the liquid, but also the rate of its impregnation into the apparatus (Lapp and Sadler, 1976).

NOTE 22: Stripping of electronic wafers is assumed to have been a cold cleaning operation which involved spraying, dipping, and/or wiping the pieces to be cleaned with solvent at room temperature.

NOTE 23: Production of 1,2,4-trichlorobenzene-containing grinding wheels involves the following steps: (1) an abrasive (often aluminum oxide, silicon carbide and/or diamond grains) is mixed with a relatively small quantity of liquid (in which 1,2,4-trichlorobenzene is a portion or all of this liquid); (2) to (1) is added a resinous powder; (3) blend (1) and (2) both mechanically and manually; (4) pour the mix into a mold and press to initially "set" the wheel; and (5) cure the mix at 160 C for 48 hours (Richards, 1980).

APPENDIX B. PROCESS SPECIFIC DATA ON 1,2,4-TRICHLOROBENZENE RELEASES

Table B-1 Quantities of 1,2,4-Trichlorobenzene-Containing Wastes Released to the Environment from Wet Processing Textile Mills in 1979 (kkg)[a]

Type of Treatment[b]	Wool Scouring[c]						Woven Fabric Finishing[d]						Knit Fabric Finishing[e]					
	% of total Wastes[f]	quantity released[g]					% of total Wastes[f]	quantity released[g]					% of total Wastes[f]	quantity released[g]				
		(T)	Water		land	air		(T)	Water		land	air		(T)	Water		land	air
			D	I					D	I					D	I		
None	35	37	6	31			41	615	41	574			51	961	66	895		
Preliminary	29	30	12	18			22	330	34	296			21	396		396		
Biological (or equivalent)	35	38	3	1	17[h]	17[h]	25	375	28	10	169[h]	169[h]	20	377	21	17	169[h]	169[h]
Advanced	0	0					1	15			15[i]		2	38			38[i]	
Unknown	0	0					11	165	132[j]	33			6	113	92[j]	21		
Total		105[k]	21	50	17	17		1,501[k]	235	913	184	169		1,885[k]	283	1,225	207	169

a) Number may not add due to rounding.

b) Preliminary refers to: neutralization, screening, equalization, heat exchange, disinfection, primary sedimentation, and/or floatation; biological or equivalent refers to: aerated and unaerated lagoons, biological filtration, activated sludge, chemical coagulation/flocculation without preceeding biological treatment; advanced refers to: activated carbon, chemical coagulation following biological treatment, ozonation, filtration, ion exchange and membrane processes; unknown means the type of treatment was not determined but for purposes of this table will refer to no treatment practice. The estimated removal efficiencies for 1,2,4-trichlorobenzene per treatment practice are: none = 0%; preliminary = 0%; biological (or equivalent) = 90%; advanced = 100%; and unknown = 0%.

c) To include: raw wool scouring, heavy scour, carbonizing, bleaching and spinning.

d) To include: simple processing - piecedyeing and printing of upholstery fabric, sheets, blankets and towels and complex processing plus desizing - desizing, scouring, bleaching, mercerizing, piecedyeing, weaving, printing and yarn dyeing of finished fabric, sheets, shirting, apparel and denim.

e) To include: simple processing - scouring, piecedyeing of apparel, outerware and car upholstery fabrics and complex processing - scouring, bleaching, printing and piecedyeing of apparel and finished fabrics.

f) Based on the assumption that all mills produce equal quantities of 1,2,4-trichlorobenzene wastes where all is initially discharged to water, the percent of total 1,2,4-trichlorobenzene-containing waste generated by mills with both this operation and type of treatment is based upon the distribution of treatment practices utilized by the surveyed wet processing textile mills that discharged 1,2,4-trichlorobenzene (EPA, 1979b).

g) (T) = total quantity of 1,2,4-trichlorobenzene released to water, land and air combined; D = 1,2,4-trichlorobenzene waste directly discharged to surface waters, I = 1,2,4-trichlorobenzene waste indirectly discharged via publicly owned treatment works; 105, 1,501 and 1,885 metric tons of 1,2,4-trichlorobenzene were used and released by wool scouring, woven fabric finishing, and knit fabric finishing operations, where (T) was calculated by multiplying % of total wastes per type of treatment times the total amount of 1,2,4-trichlorobenzene waste per operation, i.e., (for wool scouring with no treatment): (T) = .35 (143) = 50 kkg; T was calculated by multiplying (T) times the % of wastes not captured (based on control device efficiency). The quantity of 1,2,4-trichlorobenzene wastes distributed between D and I was based upon the discharge practices of the U.S. wet processing textile mills surveyed in an EPA report (1979b) and shown in Figure B2, Appendix B.

h) Based on the assumption that the 1,2,4-trichlorobenzene removed during biological (or equivalent) treatment was divided equally between land and air sinks.

i) Based on the assumption that the 1,2,4-trichlorobenzene wastes removed during advanced treatment were sent to land.

j) Based on the assumption that the 1,2,4-trichlorobenzene contained in these wastewaters, which were disposed of by an unknown means (see "U" on Table B2 in Appendix B) was sent to surface waters.

k) Values calculated by multiplying the total quantity of 1,2,4-trichlorobenzene released by the textile industry in 1979 (3,489 kkg) times the percent of textile mills performing that operation which releases 1,2,4-trichlorobenzene; i.e., 17 wool scouring mills of the total 520 mills releasing 1,2,4-trichlorobenzene = 3%; 3% of 3,489 = 105 kkg, see Table B-2 in Appendix B for total number of mills per pertinent operation.

Source: EPA, 1979b.

Table B-2. Wastewater Treatment Status - Wet Processing Mills Surveyed[a]

Mill Operation	No Treatment		Preliminary		Biological or Equivalent		Advanced		Treatment Unclassified			Totals		
	D	I	D	I	D	I	D	I	D	I	U	D	I	All Mills
Wool Scouring	1	5	2	3	4	2	0	0	0	0	0	7	10	17
Woven Fabric Finishing[b]	6	84	5	43	40	15	3	0	0	5	20	54	148	221
Knit Fabric Finishing Fabric Processing	10	135	0	59	31	24	7	0	0	3	13	48	221	282
Total	17	224	7	105	75	41	10	0	0	8	33	109	379	520

a) D refers to direct discharger, I to indirect dischargers, and U to unclssified mill
Preliminary - neutralization, screening, equalization, heat exchange, disinfection, primary sedimentation, and/or flotation
Biological or Equivalent - aerated and unaerated lagoons, biological filtration, activated sludge, chemical coagulation/flocculation without proceeding biological treatment
Advanced - activated carbon, chemical coagulation following biological treatment, ozonation, filtration, ion exchange, membrane processes, etc.

b) Includes simple processing and complex processing plus desizing.

Source: EPA, 1979b.

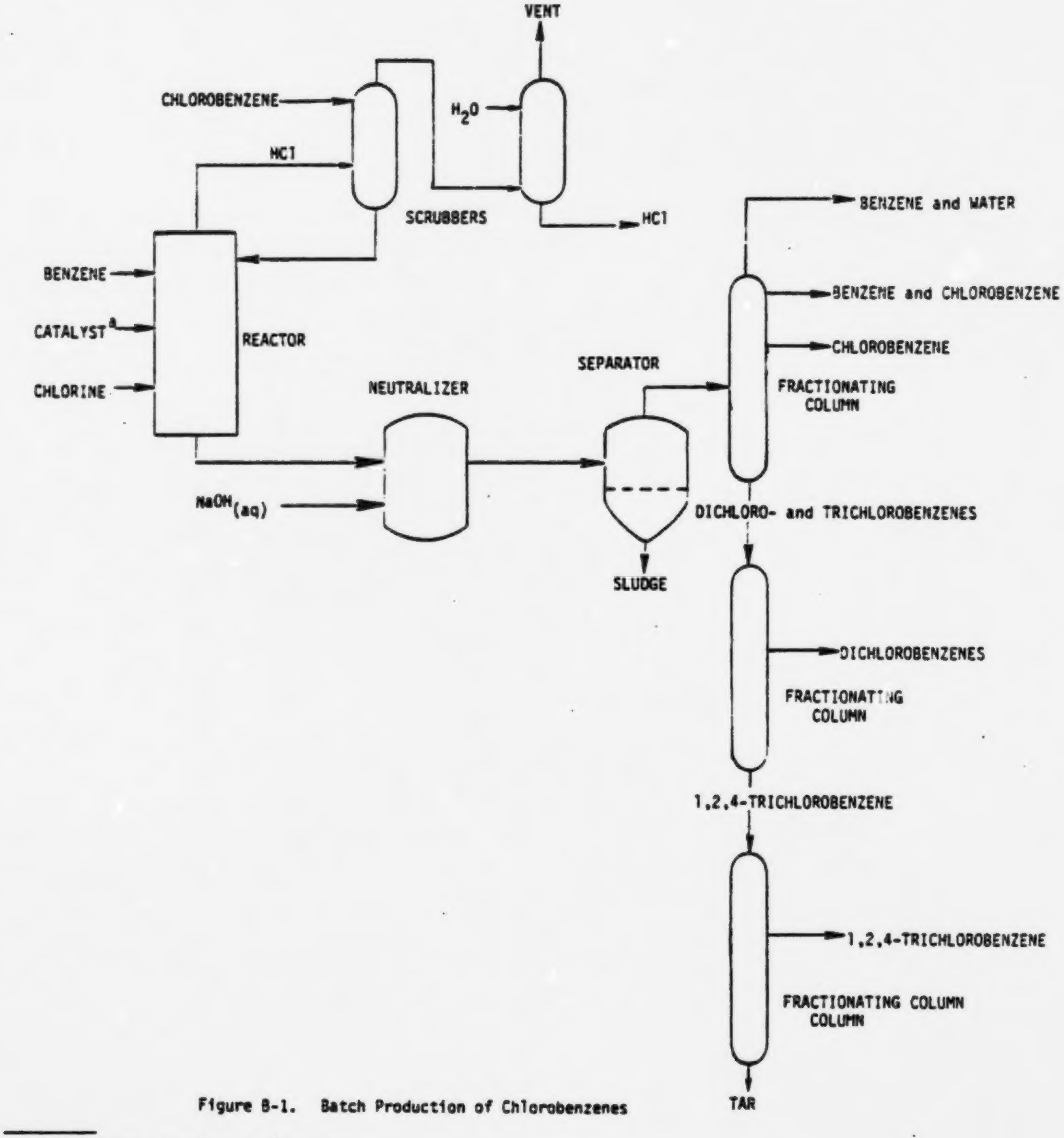
VENT
CHLOROBENZENE
H$_2$O
HCl
SCRUBBERS
HCl
BENZENE and WATER
BENZENE
BENZENE and CHLOROBENZENE
CATALYST[a]
REACTOR
CHLOROBENZENE
SEPARATOR
CHLORINE
NEUTRALIZER
FRACTIONATING COLUMN
NaOH$_{(aq)}$
DICHLORO- and TRICHLOROBENZENES
SLUDGE
DICHLOROBENZENES
FRACTIONATING COLUMN
1,2,4-TRICHLOROBENZENE
1,2,4-TRICHLOROBENZENE
FRACTIONATING COLUMN
COLUMN
TAR

Figure B-1. Batch Production of Chlorobenzenes

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a) Ferric chloride or iron filings.
Source: Lowenheim and Moran, 1975; EPA, 1977a.

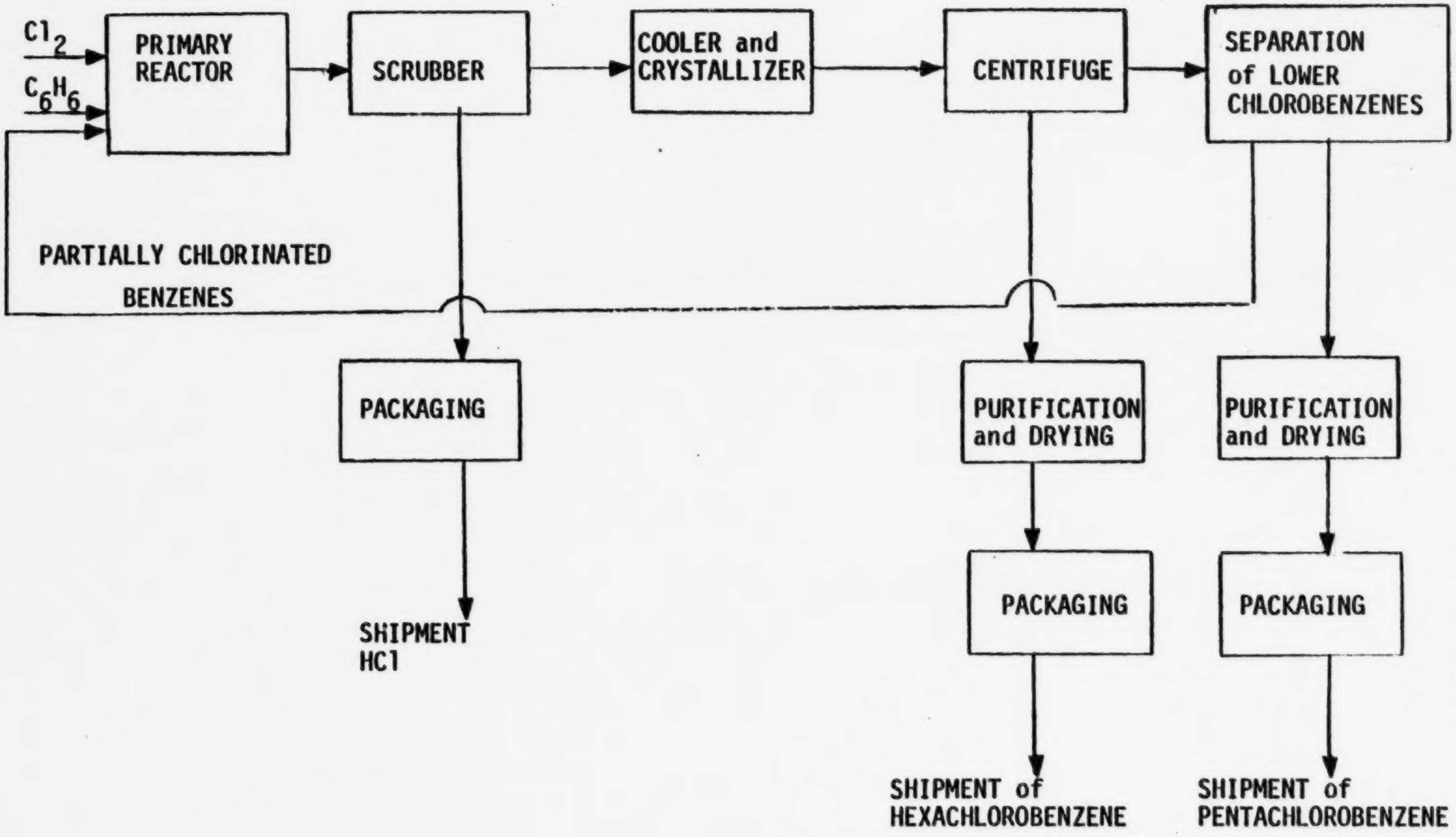
Cl_2
C_6H_6
PRIMARY REACTOR
SCRUBBER
COOLER and CRYSTALLIZER
CENTRIFUGE
SEPARATION of LOWER CHLOROBENZENES
PARTIALLY CHLORINATED BENZENES
PACKAGING
PURIFICATION and DRYING
PURIFICATION and DRYING
PACKAGING
PACKAGING
SHIPMENT HCl
SHIPMENT of HEXACHLOROBENZENE
SHIPMENT of PENTACHLOROBENZENE

Figure B-2. Production Schematic for Pentachlorobenzene by Chlorination of Benzene or Chlorobenzene (EPA, 1975b)

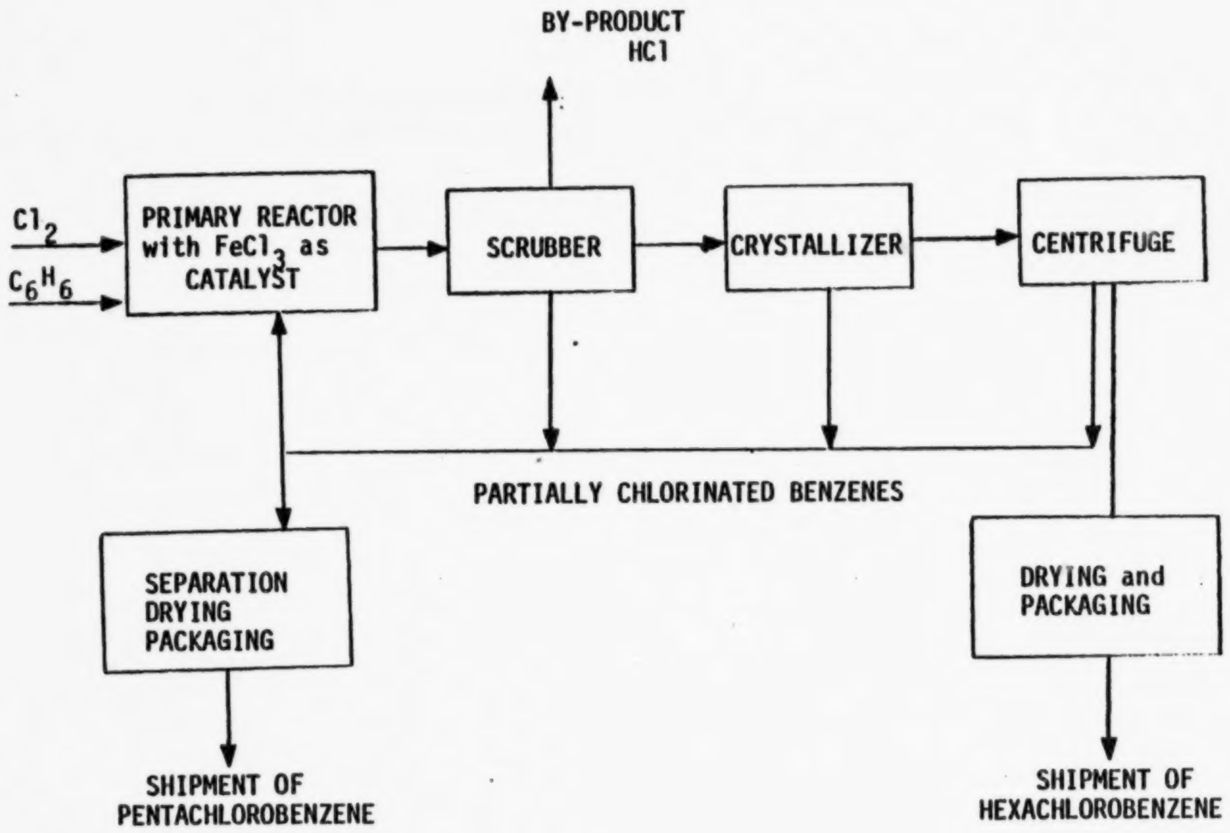
BY-PRODUCT HCl
Cl_2
C_6H_6
PRIMARY REACTOR with $FeCl_3$ as CATALYST
SCRUBBER
CRYSTALLIZER
CENTRIFUGE
PARTIALLY CHLORINATED BENZENES
SEPARATION DRYING PACKAGING
DRYING and PACKAGING
SHIPMENT OF PENTACHLOROBENZENE
SHIPMENT OF HEXACHLOROBENZENE

Figure B-3. Production Schematic for Hexachlorobenzene by Chlorination of Benzene and Chlorobenzenes (EPA, 1975b)

APPENDIX C. ESTIMATION OF VOLATILIZATION FROM WATER

Volatilization from water can be estimated using procedures described in the literature. The mathematical modeling of volatilization involves interphase exchange coefficients that depend on the chemical and physical properties of the chemical in question, the presence of other pollutants, and the physical properties of the water body and atmosphere above it. Basic factors controlling volatilization are solubility, molecular weight, and the vapor pressure of the chemical and the nature of the air-water interface through which the chemical must pass.

Because of the lack of data for most chemicals, however, estimates of volatilization rates from surface waters on the basis of mathematical data and laboratory measurements are necessarily of unknown precision. Still, comparisions of experimental results with theoretical predictions indicate that these predictive techniques generally agree with actual processes within a factor of two or three in most cases.

The methods described below have been used to estimate volatilization from natural surface water (see Section 4.12). The EXAMS model has been used to investigate behavior in natural surface water bodies, however, this method was not used as input to EXAMS. An input parameter similar to the reaeration coefficients described below is used in EXAMS to estimate volatilization; this value was obtained elsewhere (SRI 1980).

The following procedures were used to estimate the volatilization rate of a chemical. Minimum data required are:

- Chemical properties--vapor pressure, aqueous solubility, molecular weight;
- Environmental characteristics—wind speed, current speed, depth of water body;

(1) Find or estimate the Henry's Law constant H from:

$$H = P/S \quad \text{atm-m}^3/\text{mole}$$

where P = vapor pressure, atm
S = aqueous solubility, mole/m^3.

When calculating H as a ratio of vapor pressure to solubility, it is essential to have these data at about the same temperature and applicable to the same physical state of the compound. Data for pure compounds should be used because vapor pressure and solubilities of mixtures may be suspect.

(2) If $H < 3 \times 10^{-7}$ atm-m^3/mole, volatilization can be considered unimportant as an intermedia transfer mechanism and no further calculations are necessary.

(3) If $H > 3 \times 10^{-7}$ atm-m^3/mole, the chemical can be considered volatile. The nondimensional Henry's Law constant H' should be determined from:

$$H' = H/RT \tag{2}$$

where R = gas constant, 8.2×10^{-5} atm-m^3/mole K

T = temperature, K.

At 20C (293K) RT is 2.4×10^{-2} atm-m^3/mole.

(4) The liquid phase exchange coefficient k_ℓ must be estimated. This coefficient is from a method that analyzes the volatilization process on the basis of a two-layer film, one water and one air, which separates the bulk of the water body from the bulk of the air (Liss and Slater 1974).

For a low molecular weight compound ($15<M<65$),

$$k_\ell = \sqrt{44/M} \quad \text{cm/hr} \tag{3}$$

where M = molecular weight of the chemical.

If $M>65$, k_ℓ can be estimated from equations developed by Southworth (1979). Because this method is different from Equation (3), the estimated values may vary. If the average wind speed is $\leq$ 1.9 m/sec,

$$k_\ell = \left(\frac{V_{curr}^{0.969}}{Z^{0.673}}\right) \sqrt{\frac{32}{M}} \tag{4}$$

where V_{curr} = water current velocity, m/sec

Z = depth of water body, m.

If wind speed is >1.9 m/sec and <5 m/sec,

$$k_\ell = \left(\frac{V_{curr}^{0.969}}{Z^{0.673}}\right) \sqrt{\frac{32}{M}} \cdot e^{0.526\,(V_{wind}-1.9)} \quad \text{cm/hr} \tag{5}$$

where V_{wind} = windspeed, m/sec.

If wind speed is >5 m/sec, liquid phase exchange coefficients are difficult to predict and may range up to 70 cm/hr.

(5) The gas phase exchange coefficient must be estimated. This too is based on the two-film analysis. For a compound of $15<M<65$ (Liss and

Slater (1974),

$$k_g = 3000\sqrt{18/M}\ \text{cm/hr} \tag{6}$$

If M>65 (Southworth 1979),

$$k_g = 1137.5\ (V_{wind} + V_{curr})\sqrt{18/M}\ \ \text{cm/hr}\ . \tag{7}$$

(6) The Henry's Law constant and gas and liquid phase exchange coefficients are used to compute the overall liquid phase mass transfer coefficient, K_L (Liss and Slater 1974), which is an indicator of the volatilization rate:

$$K_L = \frac{(H/RT)k_g k_\ell}{(H/RT)k_g + k_\ell} = \frac{H'k_g k_\ell}{H'k_g + k_\ell}\ \ \text{cm/hr} \tag{8}$$

(7) The volatilization rate constant k_v is:

$$k_v = K_L/Z\ \text{hr}^{-1} \tag{9}$$

where Z is in cm.

(8) Assuming a first order volatilization process, the concentration in the stream in the absence of continuing inputs at the location at which volatilization occurs, is

$$c(t) = c_o e^{-k_v t} \tag{10}$$

where $c(t)$ = pollutant concentration in the water column at time t

c_o = initial pollutant concentration in the water column.

(9) The half-life in the water column for the pollutant volatilizing at a first order rate is:

$$\tau_{½} = \frac{0.69\ Z}{K_L}\ \ \text{hr.} \tag{11}$$

Another method for computing k_v for highly volatile chemicals with $H>10^{-3}$ atm-m^3/mole is based on reaeration rate coefficients (Smith and Bomberger 1977, Smith et al. 1979, Tsivoglou 1967). The following data are required:

- Ratio of reaeration rate of chemical to that of water,
- Reaeration rate of oxygen for water bodies in the environment or steamflow parameters (velocity, stream bed slope, depth).

If the oxygen reaeration rate is known for a given water body or type of water body, the volatilization rate constant for the pollutant can be estimated from (Smith and Bomberger 1979):

$$(k_v^c)_{env} = (k_v^c/k_v^o)_{lab}\,(k_v^o)_{env} \qquad (12)$$

where k_v^c = first order volatilization rate constant for the particular chemical (hr^{-1});

k_v^o = reaeration rate constant for oxygen (hr^{-1});

env = designates values applicable to environmental situations;

lab = designates laboratory measured values.

This equation applies particularly to rivers. For lakes and ponds, the following equation may be more accurate:

$$(k_v^c)_{env} = (k_v^c/k_v^o)^{1.6}_{lab}\,(k_v^o)_{env} \qquad (13)$$

Typical values of $(k_v^o)_{env}$ are given in the literature and reported by Smith et al (1979):

Water Body	$(k_v^o)_{env}$, hr^{-1}
Pond	0.0046 - 0.0096
River	0.008, 0.04 - 0.39
Lake	0.004 - 0.013

The values for ponds and lakes are speculative and depend on depth.

Mackay and Yuen (1979) present the equations listed below that correlate k_v^o with river flow velocity, depth, and slope:

Tsivoglou-Wallace: $k_v^o = 638\ V_{curr}s\ \text{hr}^{-1}$ (14)

Parkhurst-Pomeroy: $k_v^o = 1.08\ (1 + 0.17\ F^2)\ (V_{curr}s)^{0.0375}\ \text{hr}^{-1}$ (15)

Churchill et al.: $k_v^o = 0.00102 V_{curr}^{2.695}\ Z^{-3.085}\ s^{-0.823}\ \text{hr}^{-1}$ (16)

If no slope data are available:

Isaccs-Gundy: $k_v^o = 0.223 V_{curr} Z^{-1.5}\ \text{hr}^{-1}$ (17)

Langbein-Durum: $k_v^o = 0.241\ V_{curr} Z^{-1.33}\ \text{hr}^{-1}$ (18)

where V_{curr} = river flow velocity (m/s);

s = river bed slope = m drop/m run (nondimensional);

Z = river depth (m);

g = acceleration of gravity = 9,8 m/s^2.

Because none of the foregoing is clearly superior to the others, the best approach is probably to use all that are applicable and then average the results (Cohen et al. 1978). For a river 2 m deep, flowing at 1 m/sec, the reaeration rate is estimated as 0.042/hr. $(k_v^c/k_v^o)_{lab}$ is known for some chemicals (see Table C-1). If a $(k_v^c/k_v^o)_{lab}$ value is not known, one for a similar high-volatility chemical should be a reasonable substitute.

In principle, k_v^c is the same as (K_L/Z); however, due to the use of $(k_v^o)_{env}$, k_v^c has the depth and other water body characterisitics embedded within it. Therefore, no adjustment is required for use in the first order volatilization equation.

TABLE C-1

MEASURED REAERATION COEFFICIENT RATIOS FOR HIGH VOLATILITY COMPOUNDS

Compound	H atm-m³/mole	Measured k_v^c/k_v^o
Chloroform	3.8×10^{-3}	.57 ± .02 .66 ± .11
1,1-Dichloroethane	5.8×10^{-3}	.71 ± .11
Oxygen	7.2×10^{-2}	1.0
Benzo [b] thiophene	2.7×10^{-4}	.38 ± .08
Dibenzothiophene	4.4×10^{-4}	.14
Benzene	5.5×10^{-3}	.57 ± .02
Carbon dioxide		.89 ± .03
Carbon tetrachloride	2.3×10^{-2}	.63 ± .07
Dicyclopentadiene		.54 ± .02
Ethylene	8.6	.87 ± .02
Krypton		.82 ± .08
Propane		.72 ± .01
Radon		.70 ± .08
Tetrachloroethyene	8.3×10^{-3}	.52 ± .09
Trichloroethylene	1×10^{-2}	.57 ± .15

Source: Smith *et al*. (1979).

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